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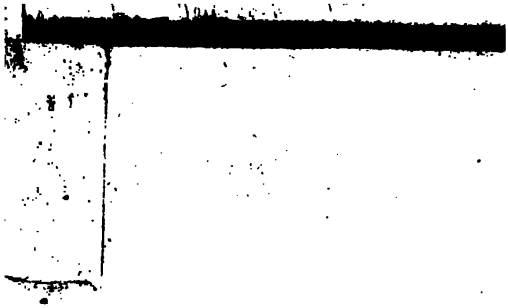

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PREFACE.

THIS work, founded on the well-known "Manual of Chemistry" of the late Professor Fownes, is intended to offer to the student commencing the study of Chemistry, an outline of the general principles of that science, and a history of the more important among the very numerous bodies which Chemical Investigations have made known to us. It has no pretensions to be considered a complete treatise on the subject, but is intended to serve as an introduction to larger and more comprehensive systematic works, and especially to prepare the student for the perusal of original memoirs, which, in conjunction with practical instruction in the laboratory, can alone afford a real acquaintance with the spirit of research and the resources of Chemical Science. It is divided into two volumes—the first relating to Chemical Physics and Inorganic Chemistry, and the second to Organic Chemistry.*

The present volume commences with a short sketch of the more important Elementary Bodies, the principal Laws of Chemical Combination, and the representation of the constitution and reactions of bodies by Symbolic Notation.

This introduction is followed by a section on CHEMICAL PHYSICS, including the determination of Densities, the mechanical properties of Gases, and the chief phenomena of Heat, Light, Electricity, and Magnetism, an elementary knowledge of which affords great assistance in the study of chemical reactions.

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* Chemistry of Carbon-Compounds, or Organic Chemistry, 12th Edition, 10*s*.

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A

MANUAL OF CHEMISTRY.

PHYSICAL AND INORGANIC.

INTRODUCTION.

THE Science of Chemistry has for its object the study of the nature and properties of the materials which enter into the composition of the earth, the sea, and the air, and of the various organised or living beings which inhabit them.

In ordinary scientific speech the term *chemical* is applied to changes which permanently affect the properties or characters of bodies, in opposition to effects termed *physical*, which are not attended by such consequences. Changes of decomposition or combination are thus easily distinguished from those temporarily brought about by heat, electricity, magnetism, and the attractive forces, whose laws and effects lie within the province of Physics.

Nearly all the objects presented by the visible world are of a compound nature, and capable of being resolved into simpler forms of matter. Thus, a piece of limestone or marble, by the application of a red heat, is decomposed into quicklime and a gaseous body, carbon dioxide. Both lime and carbon dioxide are in their turn susceptible of decomposition—though not by the action of heat alone—the former into calcium and oxygen, the latter into carbon and oxygen. Beyond this second step of decomposition the efforts of Chemistry have hitherto been found to fail; and the three bodies

calcium, carbon, and oxygen, having resisted all attempts to resolve them into simpler forms of matter, are admitted into the list of *elements;* not from an absolute belief in their real oneness of nature, but from the absence of any evidence that they contain more than one description of matter.

The elementary bodies, at present recognised, are sixty-seven in number, and about fifty of them belong to the class of *metals.* Several of these are of recent discovery, and are as yet very imperfectly known. The distinction between metals and non-metallic substances, although very convenient for purposes of description, is entirely arbitrary, the two classes not being separated by any exact line of demarcation.

The names of the elements are given in the following table. Opposite to them in the third column are placed certain numbers, which express the proportions in which they combine together, or simple multiples of those proportions; these numbers, for reasons which will be afterwards explained, are called Atomic or Indivisible Weights. In the second column are placed symbols by which these weights are denoted; these symbols are formed of the first letters of the Latin names of the elements, a second letter being added when the names of two or more elements begin with the same letter.

The names of the most important elements are distinguished by the largest and most conspicuous type; those next in importance, by small capitals; while the names of elements which are of rare occurrence, or of which our knowledge is still imperfect, are printed in ordinary type. The names with an asterisk are those of Non-metallic Elements, the others are names of Metals.

TABLE OF ELEMENTARY BODIES WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
ALUMINIUM	Al	27·3	NICKEL	Ni	58·6
ANTIMONY (Stibium)	Sb	122	Niobium	Nb	94
ARSENIC	As	74·9	**NITROGEN***	N	14·01
BARIUM	Ba	136·8	Osmium	Os	198·6
Beryllium	Be	9	**OXYGEN***	O	15·96
BISMUTH	Bi	210	PALLADIUM	Pd	106·2
BORON*	B	11	**PHOSPHORUS***	P	30·96
BROMINE*	Br	79·75	**PLATINUM**	Pt	196·7
Cadmium	Cd	111·6	**POTASSIUM** (Kalium)	K	39·04
Cæsium	Cs	133	Rhodium	Rh	104·1
CALCIUM	Ca	39·9	Rubidium	Rb	85·2
CARBON*	C	11·97	Ruthenium	Ru	103·5
Cerium	Ce	141·2	Scandium	Sc	44·9
CHLORINE*	Cl	35·37	Selenium*	Se	78
CHROMIUM	Cr	52·4	**SILICON**	Si	28
COBALT	Co	58·6	**SILVER** (Argentum)	Ag	107·66
COPPER (Cuprum)	Cu	63	**SODIUM** (Natrium)	Na	23
Didymium	D	146·6	STRONTIUM	Sr	87·2
Erbium	E	166	**SULPHUR***	S	31·98
FLUORINE*	F	19·1	Tantalum	Ta	182
Gallium	Ga	69·8	Tellurium*	Te	128
GOLD (Aurum)	Au	196·2	Terbium	Tb	148
HYDROGEN*	H	1	Thallium	Tl	203·6
Indium	In	113·4	Thorium	Th	231·5
IODINE*	I	126·53	**TIN** (Stannum)	Su	117·8
Iridium	Ir	196·7	Titanium	Ti	48
IRON (Ferrum)	Fe	55·9	TUNGSTEN, or Wolfram	W	184
Lanthanum	La	139	URANIUM	U	240
LEAD (Plumbum)	Pb	206·4	Vanadium	V	51·2
Lithium	Li	7	Ytterbium	Yb	172·5 ?
MAGNESIUM	Mg	23·94	Yttrium	Y	89
MANGANESE	Mn	54·8	**ZINC**	Zn	64·9
MERCURY (Hydrargyrum)	Hg	199·8	Zirconium	Zr	90
Molybdenum	Mo	95·6			

solid body, well known under the names of charcoal, coke, lamp-black, and plumbago, or black-lead. It occurs also naturally in the pure state, forming transparent crystals known as diamond.

Chlorine, Bromine, and Iodine exist in sea-water (hence called *Halogen-elements*, from ἁλς, the sea), in combination chiefly with sodium. Chlorine in the free state is a yellowish-green gas, bromine a red liquid, iodine a greyish-black crystalline solid. Of these elements, chlorine is by far the most abundant, its compound with sodium forming common sea-salt. Fluorine is an element closely allied in its chemical relations to the three last mentioned. It is not known in the free state, but in combination with calcium it constitutes the crystallised mineral called fluorspar.

Sulphur, a well-known substance, occurs in the free state in volcanic districts, and abundantly in various parts of the world in combination with iron, copper, lead, and other metals, forming compounds called *sulphides*. Selenium and Tellurium are rare elements, allied to sulphur, and likewise found in combination with metals.

Phosphorus, in the free state, is a highly inflammable solid body, which burns rapidly in contact with the air, being converted, by combination with oxygen, into *phosphoric acid*, a compound which, in combination with calcium, occurs very abundantly in nature, forming the minerals called phosphorite and apatite, and is the chief mineral constituent of the bones of animals. Arsenic, sometimes regarded as a metal, is an element closely allied in its chemical relations to phosphorus, and occurring in nature in combination with oxygen, sulphur, and various metals.

Silicon is a very abundant and important element, not occurring in nature in the free state, but forming, in combination with oxygen, the mineral called *silica*, which in the form of quartz, flint, and sandstone, and as a constituent of granite, gneiss, and other ancient rocks, forms a very large portion of the crust of the earth. Boron, an element analogous in many of its properties to silicon, occurs naturally in combination with oxygen, forming boric or boracic acid, which is a constituent of several minerals, and occurs somewhat abundantly in solution in certain natural waters.

Of the fifty-four metals, seven only were known in ancient times, viz., iron, copper, lead, tin, mercury, silver, and gold; of these, by far the most abundant and important is iron. Of the metals more recently discovered, the most abundant are sodium, potassium, calcium, and aluminium. Sodium, as already observed, forms, in combination with chlorine, the chief saline constituent of sea-water. Potassium, which resembles it in many respects, exists also in the sea, and is a constituent of all plants. Calcium is the metallic constituent of limestone, and aluminium of clay.

General Laws of Chemical Combination.—Chemical Nomenclature and Notation.—The compounds formed by the union of oxygen with other bodies bear the general name of oxides. They are conveniently divided into three principal groups or classes. The first division contains all those oxides which resemble in their chemical relations the oxides of potassium, sodium, silver, or lead: these are denominated alkaline or basic oxides. The oxides of the second group have properties opposed to those of the bodies mentioned; the oxides of sulphur and phosphorus may be taken as typical representatives of the class; they are called acid oxides, and are capable of uniting with the basic oxides, and forming compounds called salts. Thus, when the oxide of sulphur, called sulphuric oxide, is passed in the state of vapour over heated barium oxide, combination takes place, attended with vivid incandescence, and a salt called barium sulphate is produced, containing all the elements of the two original bodies, namely, barium, sulphur, and oxygen.

Among salts there is a particular group, namely, the hydrogen salts, containing the elements of an acid oxide and water (hydrogen oxide), which are especially distinguished as acids, because many of them possess in an eminent degree the properties to which the term acid is generally applied, such as a sour taste, corrosive action, solubility in water, and the power of reddening certain blue vegetable colours. A characteristic property of these acids, or hydrogen salts, is their power of exchanging their hydrogen for a metal presented to them in the free state, or in the form of oxide. Thus, sulphuric acid, which contains sulphur, oxygen, and hydrogen,

readily dissolves metallic zinc, the metal taking the place of the hydrogen, which is evolved as gas, and forming a salt containing sulphur, oxygen, and zinc; in fact, a *zinc sulphate*, produced from a *hydrogen sulphate* by substitution of zinc for hydrogen. The same substitution and formation of zinc sulphate take place when zinc oxide is brought into contact with sulphuric acid; but in this case the hydrogen, instead of being evolved as gas, remains combined with the oxygen derived from the zinc oxide, forming water.

A series of oxides containing quantities of oxygen in the proportion of the numbers 1, 2, 3, united with a constant quantity of another element, are distinguished as *monoxide*, *dioxide*, and *trioxide* respectively, the Greek numerals indicating the several degrees of oxidation. A compound intermediate between a monoxide and a dioxide is called a *sesquioxide*, *e.g.*:—

	Chromium.		Oxygen.
Chromium monoxide	52·4	+	16
Chromium sesquioxide	52·4	+	24
Chromium dioxide	52·4	+	32
Chromium trioxide	52·4	+	48

When a metal forms two basic or salifiable oxides, they are distinguished by adjectival terms, ending in *ous* for the lower, and *ic* for the higher degree of oxidation, *e.g.*:—

	Iron.		Oxygen.
Iron monoxide, or Ferrous oxide . .	56	+	16
Iron sesquioxide, or Ferric oxide . .	56	+	24

The salts resulting from the action of acids on these oxides are also distinguished as ferrous and ferric salts respectively.

Acid oxides of the same element, sulphur for example, are also distinguished by the terminations *ous* and *ic*, applied as above; their acids, or hydrogen salts, receive corresponding names; and the salts formed from these acids are distinguished by names ending in *ite* and *ate* respectively. Thus, for the oxides and salts of sulphur:—

	Sulphur.		Oxygen.		
Sulphurous oxide	32	+	32		
					Hydrogen.
Hydrogen sulphite, or Sulphurous acid	32	+	48	+	2
					Lead.
Lead sulphite	32	+	48	+	206·4

	Sulphur.		Oxygen.		
Sulphuric oxide	32	+	48		
					Hydrogen.
Hydrogen sulphate, or Sulphuric acid .	32	+	64	+	2
					Lead.
Lead sulphate	32	+	64	+	206·4

The acids above spoken of are oxygen-acids; and formerly it was supposed that all acids contained oxygen—that element being, indeed, regarded as the acidifying principle. At present, however, we are acquainted with many bodies which possess all the characters above specified as belonging to an acid, and yet do not contain oxygen. For example, hydrochloric acid (formerly called muriatic acid, or spirit of salt)—which is a hydrogen chloride or compound of hydrogen and chlorine—is intensely sour and corrosive; reddens litmus strongly; dissolves zinc, which drives out the hydrogen and takes its place in combination with the chlorine, forming zinc chloride; and dissolves most metallic oxides, exchanging its hydrogen for the metal, and forming a metallic chloride and water.

Bromine, iodine, and fluorine, also form, with hydrogen, acid compounds analogous in every respect to hydrochloric acid.

Compounds of chlorine, bromine, iodine, fluorine, sulphur, selenium, phosphorus, &c., with hydrogen and metals, are grouped, like the oxygen-compounds, by names ending in *ide:* thus we speak of zinc chloride, calcium fluoride, hydrogen sulphide, copper phosphide, &c. The numerical prefixes, *mono*, *di*, *tri*, &c., as also the terminations *ous* and *ic*, are applied to these compounds in the same manner as to the oxides, thus—

	Hydrogen.		Bromine.
Hydrogen bromide	1	+	80
	Potassium.		Sulphur.
Potassium monosulphide . . .	78	+	32
Potassium disulphide	78	+	64
Potassium trisulphide	78	+	96
Potassium tetrasulphide . . .	78	+	128
Potassium pentasulphide . . .	78	+	160
	Iron.		Chlorine.
Ferrous chloride	56	+	71
Ferric chloride	56	+	106·5

	Tin.		Sulphur.
Stannous sulphide	117·8	+	64
Stannic sulphide	117·8	+	128

The Latin prefixes *uni*, *bi*, *ter*, *quadro*, &c., are often used nstead of the corresponding Greek prefixes; there is no very exact rule respecting their use; but, generally speaking, it is best to employ a Greek or Latin prefix, according as the word before which t is placed is of Greek or Latin origin. Thus, *di*oxide corresponds with *bi*sulphide; on the whole, however, the Greek prefixes are most generally employed.

The composition of these oxides and sulphides affords an illustration of a law which holds good in a large number of instances of chemical combination, viz., that *when two bodies*, A *and* B, *are capable of uniting in several proportions, the several quantities of* B *which combine with a given or constant quantity of* A *stand to one another in very simple ratios.* Thus, the several quantities of sulphur which unite with a given quantity (78 parts) of potassium are to one another as the numbers

1, 2, 3, 4, 5;

and the quantities of oxygen which unite with a given quantity of chromium are as the numbers,

1,	$1\frac{1}{2}$,	2,	3,
or 2,	3,	4,	6.

It must be especially observed that no compounds are known intermediate in composition between those which are represented by these numbers. There is no oxide of chromium containing $1\frac{1}{4}$ or $1\frac{5}{8}$ or $2\frac{7}{8}$ times as much oxygen as the lowest; no sulphide of potassium the quantity of sulphur in which is expressed by any fractional multiple of the lowest. The quantities of the one element which can unite with a constant quantity of the other, increase, not continuously, but by successive and well-defined steps or increments, standing to one another, for the most part, in simple numerical ratios.

This is called the "Law of Multiples." The observation of it has led to the idea that the elementary bodies are composed of ulti-

mate or indivisible particles or atoms, each having a constant weight peculiar to itself (the atomic weights given in the table on page 3), and that combination between two elements takes place by the juxtaposition of these atoms. A collection of elementary atoms united together to form a compound constitutes a molecule, the weight of which is equal to the sum of the weights of its component atoms. Thus an atom of chlorine weighing 35·4 unites with an atom of hydrogen weighing 1, to form a molecule of hydrogen chloride weighing 36·4. An atom of oxygen weighing 16 unites with 2 atoms of hydrogen, each weighing 1, to form a molecule of water, weighing $16 + 2 . 1 = 18$. An atom of oxygen, weighing 16, unites with an atom of lead, weighing 206·4, to form a molecule of lead oxide, weighing 222·4. Two atoms of potassium, each weighing 39, unite with 1, 2, 3, 4, and 5 atoms of sulphur, each weighing 32, to form the several sulphides enumerated on page 9.

These combinations are represented symbolically by the juxtaposition of the symbols of the elementary atoms given in the table already referred to; thus the molecule of hydrogen chloride, composed of 1 atom of hydrogen and 1 atom of chlorine, is represented by the symbol or formula HCl; that of water (2 atoms of hydrogen and 1 atom of oxygen), by HHO, or more shortly H_2O. In like manner the different oxides, sulphides, acids and salts above enumerated, are represented symbolically as follows:—

Chromium monoxide . . .	CrO	
Chromium sesquioxide . . .	CrCrOOO	or Cr_2O_3
Chromium dioxide . . .	CrOO	or $Cr O_2$
Chromium trioxide . . .	CrOOO	or $Cr O_3$
Sulphurous oxide	SOO	or SO_2
Hydrogen sulphite or Sulphurous acid	SOOOHH	or SO_3H_2
Lead sulphite	SOOOPb	or SO_3Pb
Potassium monosulphide . .	KKS	or K_2S
Potassium disulphide . . .	KKSS	or K_2S_2
Potassium trisulphide . . .	KKSSS	or K_2S_3
Potassium tetrasulphide . .	KKSSSS	or K_2S_4
Potassium pentasulphide . .	KKSSSSS	or K_2S_5

3. Action of zinc on hydrogen chloride, producing zinc chloride and free hydrogen—

$$2HCl + Zn = ZnCl_2 + H_2.$$

4. Action of zinc on hydrogen sulphate, producing zinc sulphate and hydrogen—

$$H_2SO_4 + Zn = ZnSO_4 + H_2.$$

5. Action of zinc oxide on hydrogen chloride or sulphate, producing zinc chloride or sulphate and water—

$$2HCl + ZnO = ZnCl_2 + H_2O,$$

and

$$H_2SO_4 + ZnO = ZnSO_4 + H_2O.$$

It need scarcely be observed that the test of correctness of such an equation is, that the number of atoms of each element on one side should be equal to the number of atoms of the same element on the other side.

Any such symbolical equation may be converted into a numerical equation, by substituting for each of the chemical symbols its numerical value from the table of atomic weights.

The laws of chemical action and their expression by symbols and equations will receive abundant illustration in the special descriptions which follow; their general consideration will also be more fully developed in a subsequent part of the work.

Before proceeding with the detailed description of the several elements and their compounds, it is desirable to give a short sketch of certain branches of Physical Science, viz., the mechanical constitution of gases, and the chief phenomena of heat, light, electricity, and magnetism, the partial study of which greatly facilitates the understanding of chemical reactions.

PART I.—PHYSICS.

OF DENSITY AND SPECIFIC GRAVITY.

It is of great importance to understand clearly what is meant by the terms *density* and *specific gravity*. By the *density of a body* is meant its *mass*, or *quantity of matter*, compared with the mass or quantity of matter of an *equal volume* of some standard body, arbitrarily chosen. *Specific gravity* denotes the *weight* of a body, —or the force with which it tends to fall to the earth—as compared with the weight of an equal bulk, or volume, of the standard body, which is reckoned as unity.* In all cases of solids and liquids the standard of unity adopted in this country is pure water at the temperature of 15·5° C. (60° Fahr.). Anything else might have been chosen; there is nothing in water to render its adoption for the purpose mentioned indispensable: it is simply taken for the sake of convenience, being always at hand, and easily obtained in a state of perfect purity. An ordinary expression of specific weight, therefore, is a number expressing how many times the weight of an equal bulk of water is contained in the weight of the substance spoken of. If, for example, we say that concentrated oil of vitriol has a specific gravity equal to 1·85, or that perfectly pure alcohol has a density of 0·794 at 15·5° C., we mean that equal bulks of these two liquids and of distilled water possess weights in the proportion of the numbers 1·85, 0·794, and 1; or 1850, 794, and 1000. It is necessary to be particular about the temperature, for, as will be hereafter shown, liquids are extremely expansible by heat; otherwise a constant bulk of the same liquid will not retain a constant weight. It will be proper to begin with the description of the mode in which the specific gravity of liquids is determined: this is the simplest case, and the one which best illustrates the general principle.

To find the specific gravity of any particular liquid compared with that of water, it is only requisite to weigh equal bulks at the standard temperature, and then divide the weight of the liquid by

* In other words, density means comparative *mass*, and specific gravity comparative *weight*. These expressions, although really relating to distinct things, are often used indifferently in chemical writings, and without practical inconvenience, since mass and weight are directly proportional to each other.

the weight of the water; the quotient will be greater or less than unity, as the liquid experimented on is heavier or lighter than water. Now, to weigh equal bulks of two liquids, the simplest and best method is clearly to weigh them in succession in the same vessel, taking care that it is equally full on both occasions.

The vessel commonly used for this purpose is a small glass bottle provided with a perforated conical glass stopper, very accurately fitted by grinding. By completely filling the bottle with liquid, and carefully removing the portion of liquid which is displaced when the stopper is inserted, an unalterable measure is obtained. The least possible quantity of grease applied to the stopper greatly promotes the exact fitting.

When the chemist has only a very small quantity of a liquid at his disposal, and wishes not to lose it, the little glass vessel (fig. 2) is particularly useful. It is formed by blowing a bulb on a glass tube. On that portion of the tube which is narrowed by drawing

Fig. 1.

Fig. 2.

the tube out over a lamp, a fine scratch is made with a diamond. The bulb is filled up to this mark with the liquid whilst it stands in water, the temperature of which is exactly known. A very fine funnel is used for filling the bulb, the stem of the funnel being drawn out so as to enter the tube, and the upper opening of the funnel being small enough to be closed by the finger. The glass

stopper is wanted only as a guard, and does not require to fit perfectly.

Another form of apparatus for determining the specific gravity of liquids, devised by Dr. Sprengel, consists of an elongated U-tube (fig. 3), the ends of which terminate in the two capillary tubes, *a*, *b*,

Fig. 3.

Fig. 4.

bent at right angles in opposite directions. The shorter one, *a*, is a good deal narrower (at least towards the end) than the longer one, the inner diameter of which is about half a millimeter. The horizontal part of this wider tube is marked near the bend with a fine line, *b*. The U-tube is filled by suction—the little bulb-apparatus (fig. 4) having been previously attached to the narrow capillary tube by a piece of india-rubber tubing—then detached from the bulb, placed in water almost up to the bends of the capillary tubes, left there till it has assumed the temperature of the water, and, after careful adjustment of the volume of the liquid up to the mark *b* in the wider capillary tube, it is taken out, dried, and weighed.

The determination of the specific gravity of a solid body is also made according to the principles above explained, and may be performed with the specific-gravity bottle (fig. 1). The bottle is first weighed full of water; the solid is then placed in the same pan of the balance, and its weight is determined; finally, the solid is put into the bottle, displacing an equal bulk of water, the weight of which is determined by the loss on again weighing. Thus, the weights of the solid and that of an equal bulk of water, are obtained. The former divided by the latter gives the specific gravity.

which experience shows is without action. Alcohol or oil of turpentine may generally be used when water is inadmissible. Suppose, for instance, the specific gravity of crystallised sugar is required, we proceed in the following way :—The specific gravity of the oil of turpentine is first determined ; let it be 0·87 ; the sugar is next weighed in the air, then suspended by a horsehair, and weighed in the oil ; the difference is the weight of an equal bulk of the latter ; a simple calculation gives the weight of a corresponding volume of water :—

Weight of sugar in air	400	grains.
Weight of sugar in oil of turpentine . . .	182·5	,,
Weight of equal bulk of oil of turpentine .	217·5	,,

$$87 : 100 = 217{\cdot}5 : 250,$$

the weight of an equal bulk of water : hence the specific gravity of the sugar,—

$$\frac{400}{250} = 1{\cdot}6.$$

If the substance to be examined consists of small pieces, or of powder, the method first described, namely, that of the specific gravity bottle, can alone be used.

By this method the specific gravities of metals in powder, metallic oxides, and other compounds, and salts of all descriptions, may be readily determined. Oil of turpentine may be used with most soluble salts. The crystals should be crushed or roughly powdered to avoid errors arising from cavities in their substance.

The specific gravity of a solid can also be readily found by immersing it in a transparent liquid, the density of which has been so adjusted that the solid body remains indifferently at whatever depth it may be placed. The specific gravity of the liquid must now be determined, and it will, of course, be the same as that of the solid. It is necessary that the liquid chosen for this experiment do not dissolve or in any way act upon the solid. Solutions of mercuric nitrate, or corrosive sublimate, can be used for bodies heavier than water, whilst certain oils, and essences, and mixtures of alcohol and water, can be conveniently employed for such substances as have a lower specific gravity than water. This method is not only adapted to the exact determination of specific gravities, but also serves in many cases as a means of readily distinguishing substances much resembling one another. Suppose, for instance, a solution of mercuric nitrate to have a specific gravity 3 ; a red amethyst (2·67) will then float upon, and a topaz of the same colour (3·55) will sink in this liquid.

Hydrometers.—The theorem of Archimedes affords the key to the general doctrine of the equilibrium of floating bodies, of which an

application is made in the common hydrometer,—an instrument for finding the specific gravities of liquids in a very easy and expeditious manner.

When a solid body is placed upon the surface of a liquid specifically heavier than itself, it sinks down until it displaces a quantity of liquid equal to its own weight, at which point it floats. Thus, in the case of a substance floating in water, whose specific weight is one-half that of the liquid, the position of equilibrium will involve the immersion of exactly one-half of the body, inasmuch as its whole weight is counterpoised by a quantity of water equal to half its volume. If the same body were put into a liquid of one-half the specific gravity of water, if such could be found, it would then sink beneath the surface, and remain indifferently in any part. A floating body of known specific gravity may thus be used as an indicator of the specific gravity of a liquid. In this manner little glass beads (fig. 6) of known specific gravities are sometimes employed in the arts to ascertain in a rude manner the specific gravity of liquids; the one that floats indifferently beneath the surface, without either sinking or rising, has of course the same specific gravity as the liquid itself; this is pointed out by the number marked upon the bead.

Fig. 6.

Fig. 7.

The hydrometer (fig. 7) in general use consists of a floating vessel of thin metal or glass, having a weight beneath to maintain it in an upright position, and a stem above bearing a divided scale. The liquid to be tried is put into a small narrow jar, and the instrument floated in it. It is obvious that the denser the liquid, the higher will the hydrometer float, because a smaller displacement of liquid will counterbalance its weight. For the same reason, in a liquid of less density, it sinks deeper. The hydrometer comes to rest almost immediately, and then the mark on the stem at the fluid-level may be read off.

Very extensive use is made of instruments of this kind in the arts: they sometimes bear different names, according to the kind of liquid for which they are intended; but the principle is the same in all. The graduation is very commonly arbitrary, two or three different scales being unfortunately used. These may be sometimes reduced, however, to the true numbers expressing the specific gravity by the aid of tables of comparison drawn up for the purpose. (*See* Appendix.) Tables are likewise used to reduce the readings of the hydrometer at any temperature to those of the normal temperature.

It is much better, however, to use a hydrometer having the true scale of specific gravities marked upon its stem. To graduate such an instrument, a sufficient number of standard points may be determined by immersing it in liquids of known specific gravity, and the small interval between these points divided into equal parts.*

The determination of the specific gravity of gases and vapours of volatile liquids is a problem of very great practical importance to the chemist: the theory of the operation is as simple as when liquids themselves are concerned, but the processes are much more delicate, and involve certain corrections for differences of temperature and pressure, founded on principles yet to be discussed. It will be proper therefore to defer the consideration of these matters for the present.

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* For an accurate method of dividing the hydrometer scale when only a few points are determined by actual observation, see the article "Hydrometer," by the late Professor Jevons, in Watts's *Dictionary of Chemistry*, vol. iii, p. 206.

THE PHYSICAL CONSTITUTION OF THE ATMOSPHERE, AND OF GASES IN GENERAL.

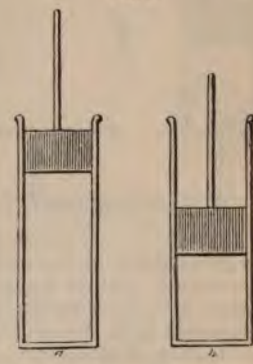
It requires some little abstraction of mind to realise completely the condition in which all things at the surface of the earth exist. We live at the bottom of an immense ocean of gaseous matter, which envelopes everything, and presses upon everything with a force which appears, at first sight, perfectly incredible, but whose actual amount admits of easy proof.

Gravity being, so far as is known, common to all matter, it is natural to expect that gases, being material substances, should be acted upon by the earth's attraction, as well as solids and liquids. This is really the case, and the result is the weight or pressure of the atmosphere, which is nothing more than the effect of the attraction of the earth on the particles of air.

Before describing the leading phenomena of the atmospheric pressure, it is necessary to notice one very remarkable feature in the physical constitution of gases, upon which depends the principle of the air-pump.

Gases are in the highest degree elastic; the volume or space which a gas occupies depends upon the pressure exerted upon it. Let the reader imagine a cylinder, *a*, closed at the bottom, in which moves a piston air-tight, so that no air can escape between the piston and the cylinder. Suppose now the piston be pressed downwards with a certain force; the air beneath it will be compressed into a smaller bulk, the amount of this compression depending on the force applied; if the power be sufficient, the bulk of the gas may be thus diminished to one hundredth part or less. When the pressure is removed, the elasticity or *tension*, as it is called, of the included air or gas, will immediately force up the piston until it arrives at its first position.

Fig. 8.

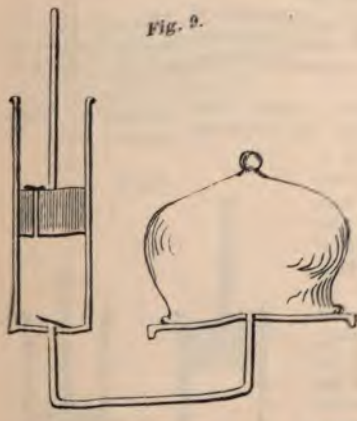


Again, take fig. 8, *b*, and suppose the piston to stand about the middle of the cylinder, having air beneath in its usual state. If the piston be now drawn upwards, the air below will expand, so as to fill completely the increased space, and this to an apparently unlimited extent. A volume of air, which, under ordinary circumstances, occupies the bulk of a cubic inch, might, by the removal of the pressure upon it, be made to expand to the capacity of a whole

room, while a renewal of the former pressure would be attended a shrinking down of the air to its former bulk. The smallest p tion of gas introduced into a large exhausted vessel becomes at o diffused through the whole space, an equal quantity being prese in every part; the vessel is *full* although the gas is in a state extreme tenuity. This power of expansion which air possesses m have, and probably has, in reality, a limit; but the limit is nev reached in practice. We are quite safe in the assumption, tha for all purposes of experiment, however refined, air is perfectl elastic.

The Air-pump.—The ordinary air-pump, shown in section in fig. 9, consists essentially of a metallic cylinder, in which moves a tightly-fitting piston, by the aid of its rod. The bottom of the cylinder communicates with the vessel to be exhausted, and is furnished with a valve opening upwards. A similar valve, also opening upwards, is fitted to the piston: these valves are made with slips of oiled silk. When the piston is raised from the bottom of the cylinder, the space left beneath it must be void of air, since the piston-valve opens only in one direction; the air within the receiver having on that side nothing to oppose its elastic power but the weight of the little valve, lifts the latter, and escapes into the cylinder. So soon as the piston begins to descend, the lower valve closes, by its own weight, or by the pressure transmitted from above, and communication with the receiver is cut off. As the descent of the piston continues, the air enclosed in the cylinder becomes compressed, its elasticity is increased, and at length it forces open the upper valve, and escapes into the atmosphere. In this manner a cylinder full of air is removed from the receiver at every stroke of the pump. During the descent of the piston, the upper valve remains open, and the lower closed, and the reverse during the opposite movement.

Fig. 9.



In practice, it is very convenient to have two such barrels or cylinders, arranged side by side, the piston-rods of which are formed into racks, having a pinion or small-toothed wheel between them, moved by a winch. By this contrivance the operation of exhaustion is much facilitated, and the labour lessened. The arrangement is shown in fig. 10.

Fig. 10.

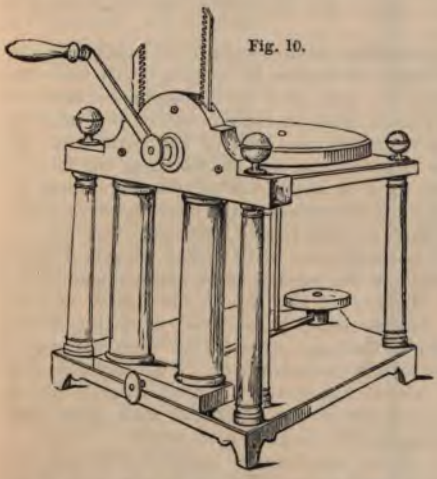


Fig. 11.

Atmospheric Pressure—The Barometer.—Air has weight; a light flask or globe of glass, furnished with a stop-cock and exhausted by the air-pump, weighs considerably less than when full of air. If the capacity of the vessel be equal to 100 cubic inches, this difference may amount to nearly 30 grains.

After what has been said on the subject of fluid pressure, it will scarcely be necessary to observe that the law of equality of pressure in all directions also holds good in the case of the atmosphere. The perfect mobility of the particles of air permits the transmission of the force generated by their gravity. The sides and bottom of an exhausted vessel are pressed upon with as much force as the top.

If a glass tube of considerable length could be perfectly exhausted of air, and then held in an upright position, with one of its ends dipping into a vessel of liquid, the latter, on being allowed access to the tube, would rise in its interior until the weight of the

column balanced the pressure of the air upon the surface of the liquid. Now, if the density of this liquid were known, and the height and area of the column measured, means would be furnished for exactly estimating the amount of pressure exerted by the atmosphere. Such an instrument is the barometer. To construct it, a straight glass tube, 36 inches long, is sealed by the blowpipe flame at one end; it is then filled with clean, dry mercury, care being taken to displace all air-bubbles, the open end is stopped with a finger, and the tube is inverted in a basin of mercury. On removing the finger, the mercury falls away from the top of the tube, until it stands at the height of about 30 inches above the level of that in the basin. Here it remains supported by, and balancing the atmospheric pressure, the space above the mercury in the tube being of necessity empty.

The pressure of the atmosphere is thus seen to be capable of sustaining a column of mercury 30 inches in height, or thereabouts. Now such a column, having an area of 1 inch, weighs between 14 and 15 lbs.: consequently such must be the amount of the pressure exerted by the air upon every square inch of the surface of the earth, and of the objects situated thereon, at least near the level of the sea. This enormous force is borne without inconvenience by the animal frame, by reason of its perfect uniformity in every direction; and it may be doubled, or even tripled, without injury.

A barometer may be constructed with other liquids besides mercury; but, as the height of the column must always bear an inverse proportion to the density of the liquid, the length of tube required will be often considerable; in the case of water it will exceed 33 feet. It is seldom that any other liquid than mercury is employed in the construction of this instrument. The Royal Society of London possessed a water barometer at their apartments at Somerset House. Its construction was attended with great difficulties, and it was found impossible to keep it in repair.

Sprengel's Air-pump.—If an aperture be made in the top of a barometer tube, the mercury will sink, and draw in air; and if the experiment be so arranged as to allow air to enter along with the mercury, and the supply of air is limited, while that of the mercury is unlimited, the air will be carried away and a vacuum produced. On this principle, Dr. Sprengel has contrived an apparatus by which a very complete exhaustion may be obtained. *cd* (fig. 12) is a glass tube longer than a barometer, open at both ends, and connected, by means of india-rubber tubing, with a funnel A filled with mercury, and supported on a stand. Mercury is allowed to fall through this tube at a rate regulated by a clamp at *c;* the lower end of the tube *cd* fits into the flask B, which has a spout at its side, a little higher than the lower end of the tube *cd;* the upper part of this tube has a branch at *x*, to which a receiver R can be tightly fixed. When the clamp at *c* is opened, the first portion of the mercury that runs out closes the tube and prevents air from entering below. As the mercury is allowed to run down, the exhaustion begins, and the

whole length of the tube from x to d is filled with cylinders of air and mercury having a downward motion. Air and mercury escape through the spout of the bulb B, below which is placed a basin H to receive the mercury; and this mercury is poured back from time to time into the funnel A, to be repassed through the tube till the exhaustion is complete. As this point is approached, the enclosed air between the mercury cylinders is seen to diminish, until the lower part of cd forms a continuous column of mercury about 30 inches high. The operation is complete when the column of mercury is quite free from air, and a drop of mercury falls on the top of it without enclosing the smallest air-bubble. The height of the column is then equal to that of the mercury in the barometer; in other words, the apparatus is a barometer whose vacuum is the receiver R. It may be advantageously combined with an exhausting syringe, which removes the greater part of the air, the exhaustion being then completed as above.

Fig. 12.

Relations between Pressure, Elasticity, and Volume of Gases.—It will now be necessary to consider a most important law which connects the volume occupied by a gas with the pressure made upon it, and is thus expressed:—

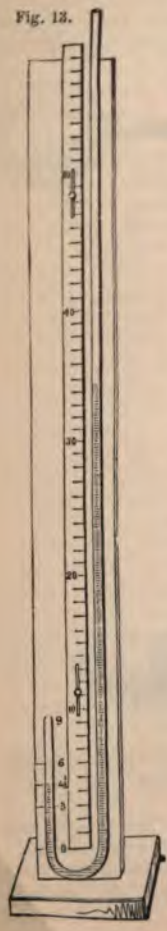
The volume of gas is *inversely* as the pressure; the density and elastic force are *directly* as the pressure, and *inversely* as the volume.

For instance, 100 cubic inches of gas under a pressure of 30 inches of mercury would expand to 200 cubic inches were the pressure reduced to one-half, and shrink, on the contrary, to 50 cubic inches

if the original pressure were doubled. The change of density must necessarily be in inverse proportion to that of the volume, and the elastic force follows the same rule.

This, which is usually called the law of Mariotte, though really discovered by Boyle (1661), is easily demonstrable by direct experiment. A glass tube about 7 feet long, is closed at one end, and bent into the form represented in fig. 13, the open limb of the syphon being the longer. It is next attached to a board furnished with a movable scale of inches, and enough mercury is introduced to fill the bend, the level being evenly adjusted, and marked upon the board. Mercury is now poured into the tube until the enclosed air is reduced to one-half of its former volume; and on applying the scale, it will be found that the level of the mercury in the open part of the tube stands very nearly 30 inches above that in the closed portion. The pressure of an additional "atmosphere" has consequently reduced the bulk of the contained air to one-half. If the experiment be still continued until the volume of air is reduced to a third, it will be found that the column measures 60 inches, and so in like proportion as far as the experiment is carried.

Fig. 13.



The above instrument is better adapted for illustration of the principle than for furnishing rigorous proof of the law. This has, however, been done. MM. Arago and Dulong published, in the year 1830, an account of experiments made by them in Paris, in which the law in question had been verified to the extent of twenty-seven atmospheres. With rarefied air also, of whatever degree of rarefaction, the law has been found true.

All gases are alike subject to this law, and all vapours of volatile liquids, when remote from their points of liquefaction.* It is a matter of the greatest importance in practical chemistry, since it gives the means of making corrections for pressure, or determining by calculation the change of volume which a gas would suffer by any given change of external pressure.

Let it be required, for example, to solve the following problem: We have 100 cubic inches of

* Near the liquefying point the law no longer holds; the volume diminishes *more rapidly* than the theory indicates, a smaller amount of pressure being then sufficient. (See further, p. 60.)

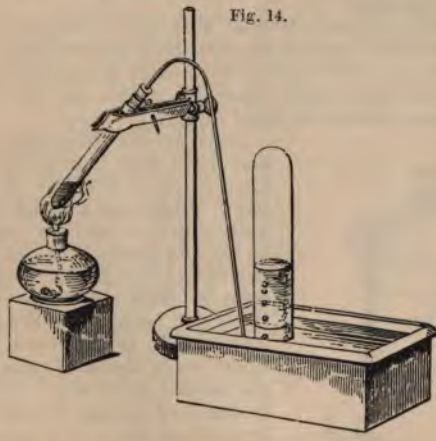
gas in a graduated jar, the barometer standing at 29 inches; how many cubic inches will it occupy when the column rises to 30 inches? Now the volume must be inversely as the pressure: consequently a change of pressure in the proportion of 29 to 30 must be accompanied by a change of volume in the proportion of 30 to 29, the 30 cubic inches of gas contracting to 29 cubic inches under the conditions imagined. Hence the answer—

$$30 : 29 = 100 : 96{\cdot}67 \text{ cubic inches.}$$

The reverse of the operation will be obvious. The pupil will do well to familiarise himself with the simple calculations of correction for pressure.

Collection, Transference, and Preservation of Gases.—The management of gases is of great importance to the chemical student. We may illustrate it by describing the preparation of oxygen gas from the red oxide of mercury. This substance is placed in a short tube of hard glass, to which is fitted a perforated cork, furnished with a piece of narrow glass tube, bent as in fig. 14. The heat of a spirit-lamp or gas-lamp being applied to the substance, decomposition speedily commences, and globules of metallic mercury collect in the cool part of the wide tube, while gas issues in considerable quantity from the apparatus. This gas is collected and examined by the aid of the pneumatic trough, which consists of a vessel of water provided with a shelf, upon

Fig. 14.



which stand the jars or bottles destined to receive the gas, filled with water and inverted. By keeping the level of the liquid

above the mouth of the jar, the water is retained in the latter by atmospheric pressure, and entrance of air is prevented. When the jar is brought over the extremity of the gas-delivery tube, the bubbles of gas, rising through the water, collect in the upper part of the jar, and displace the liquid. As soon as one jar is filled, it may be removed, still keeping its mouth below the water-level, and another substituted.

The water-trough is one of the most indispensable articles of the laboratory, and by its aid all experiments on gases are carried on when the gases themselves are not sensibly acted on by water. The trough is best constructed of japanned copper, the form and dimensions being regulated by the magnitude of the jars. It should have a firm shelf, so arranged as to be always about an inch below the level of the water, and in the shelf a groove should be made about half an inch in width and depth, to admit the extremity of the gas-delivery tube, which stands firmly on the shelf.

For gases which are easily soluble in water, such as hydrogen chloride and ammonia, a smaller trough is used, made of hard wood, and filled with mercury.

Gases are transferred from jar to jar with the utmost facility, by first filling the vessel into which the gas is to be passed, with water, inverting it, carefully retaining its mouth below the water-level, and then bringing beneath it the aperture of the jar containing the gas. On gently inclining the latter, the gas passes by a kind of inverted decantation into the second vessel. When the latter is narrow, a funnel may be placed loosely in its neck, by which loss of gas will be prevented.

A jar wholly or partially filled with gas at the pneumatic trough may be removed by placing beneath it a shallow basin, or even a common plate, so as to carry away enough water to cover the edge of the jar; and many gases, especially oxygen, may be so preserved for many hours without material injury.

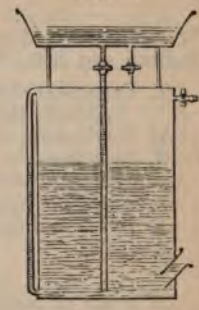
Fig. 15.

Gas-jars are often capped at the top, and fitted with a stop-cock for transferring gas to bladders or caoutchouc bags. When such a vessel is to be filled with water, it may be slowly sunk in an upright position in the well of the pneumatic trough, the stop-cock being open to allow the air to escape, until the water reaches the brass cap. The cock is then to be turned, and the jar lifted upon the shelf, and filled with gas in the usual way. If the trough be not deep enough for this method of proceeding, the mouth may be applied to the stop-cock, and the vessel filled by sucking out the air until the water rises to the cap. In all cases it is

proper to avoid as much as possible wetting the stop-cocks and other brass apparatus.

The late Mr. Pepys contrived an admirable piece of apparatus for storing and retaining large quantities of gas. It consists of a drum or reservoir of sheet copper, surmounted by a shallow trough or cistern, the communication between the two being made by a couple of tubes furnished with stop-cocks, one of which passes nearly to the bottom of the drum, as shown in fig. 16. A short wide open tube is inserted obliquely near the bottom of the vessel, into which a plug may be tightly screwed. A stop-cock near the top serves to transfer gas to a bladder or tube-apparatus. A glass water-gauge affixed to the side of the drum, and communicating with both top and bottom, indicates the level of the liquid within.

Fig. 16.



To use the gas-holder, the plug is first to be screwed into the lower opening, and the drum completely filled with water. All three stop-cocks are then to be closed and the plug removed. The pressure of the atmosphere retains the water in the gas-holder, and if no air-leakage occurs, the escape of water is inconsiderable. The extremity of the delivery-tube is now to be well pushed through the open aperture into the drum, so that the bubbles of gas may rise without hindrance to the upper part, displacing the water, which flows out in the same proportion into a vessel placed for its reception. When the drum is filled, or enough gas has been collected, the tube is withdrawn and the plug screwed into its place.

When a portion of the gas is to be transferred to a jar, the latter is to be filled with water at the pneumatic trough, carried by the help of a basin or plate to the cistern of the gas-holder, and placed over the shorter tube. On opening the cock of the neighbouring tube, the pressure of the column of water will cause compression of the gas, and increase its elastic force, so that, on gently turning the cock beneath the jar, it will ascend into the latter in a rapid stream of bubbles. The jar, when filled, may again have the plate slipped beneath it, and may then be easily removed.

Fig. 17.

HEAT.

It will be convenient to consider the subject of heat under several sections, and in the following order :—

1. Expansion of bodies, or effects of variations of temperature in altering their dimensions.
2. Conduction, or transmission of heat.
3. Specific heat.
4. Change of state.
5. Sources of heat.
6. Dynamical theory of heat.

Expansion.

If a bar of metal of such magnitude as to fit accurately to a gauge, when cold, be heated considerably, and again applied to the gauge, it will be found to have become enlarged in all its dimensions. When cold, it will once more enter the gauge.

Again, if a quantity of liquid contained in a glass bulb furnished with a narrow neck, be plunged into hot water, or exposed to any

Fig. 18.

Fig. 19.

Fig. 20.

other source of heat, the liquid will mount in the stem, showing that its volume has been increased. The bulb, however, has likewise expanded by the heat, and its capacity has consequently been augmented. The rise of the liquid in the tube, therefore, denotes the difference between these two expansions.

Or, if a portion of air be confined in any vessel, the application of a slight degree of heat will suffice to make it occupy a space sensibly larger.

This most general of all the effects of heat furnishes in the outset a principle, by the aid of which an instrument can be constructed

capable of taking cognisance of changes of temperature in a manner equally accurate and convenient: such an instrument is the thermometer.

A capillary glass tube is chosen, of uniform diameter; one extremity is closed and expanded into a bulb, by the aid of the blow-pipe flame, and the other somewhat drawn out, and left open. The bulb is now cautiously heated by a spirit-lamp, and the open extremity plunged into a vessel of mercury, a portion of which rises into the bulb when the latter cools, replacing the air which had been expanded and driven out by the heat. By again applying the flame, and causing this mercury to boil, the remainder of the air is easily expelled, and the whole space filled with mercurial vapour. The open end of the tube must now be immediately plunged into the vessel filled with mercury. As the metallic vapours condense, the pressure of the external air forces the liquid metal into the instrument, until finally the tube is completely filled with mercury. The thermometer thus filled is now to be heated until so much mercury has been driven out by the expansion of the remainder, that its level in the tube shall stand at common temperatures at the point required. This being satisfactorily adjusted, the heat is once more applied, until the column rises quite to the top; and then the extremity of the tube is hermetically sealed by the blow-pipe. The retraction of the mercury on cooling now leaves an empty space, which is essential to the perfection of the instrument.

Fig. 21.

The thermometer has yet to be graduated; and to make its indications comparable with those of other instruments, a scale, having at the least two fixed points, must be adapted to it.

It has been observed, that the temperature of melting ice, that is to say, of a mixture of ice and water, is always constant; a thermometer, already graduated, plunged into such a mixture, always marks the same degree of temperature, and a simple tube filled in the manner described and so treated, exhibits the same effect in the unchanged height of the little mercurial column, when tried from day to day. The freezing point of water, or melting point of ice, constitutes then one of the invariable temperatures demanded.

Another is to be found in the boiling point of water, or, more accurately, in the temperature of steam which rises from boiling water. In order to give this temperature, which remains perfectly constant whilst the barometic pressure is constant, to the mercury of the thermometer, distilled water is made to boil in a glass vessel

with a long neck, when the pressure is at 30 inches (fig. 20). The thermometer is then so placed that all the mercury is surrounded with steam. It quickly rises to a fixed point, and there it remains as long as the water boils, and the height of the barometer is unchanged.

The tube having been carefully marked with a file at these two points, it remains to divide the interval into degrees: this division is entirely arbitrary. The scale now most generally employed is the Centigrade, in which the space is divided into 100 parts, the zero being placed at the melting point of ice. The scale is continued above and below these points, numbers below 0 being distinguished by the negative sign.

In England the division of Fahrenheit is still in use: the above mentioned space is divided into 180 degrees; but the zero, instead of starting from the melting point of ice, is placed 32 degrees below it, so that the temperature of ebullition is expressed by 212°.

The scale of Reaumur is nearly confined to a few places in the north of Germany and to Russia: in this scale the melting point of ice is made 0°, and the boiling point of water 80°.

It is unfortunate that a uniform system has not been generally adopted in graduating thermometers: this would render unnecessary the labour which now so frequently has to be performed of translating the language of one scale into that of another. To effect this, presents, however, no great difficulty. Let it be required, for example, to know the degree of Fahrenheit's scale which corresponds to 60° C.

$$100° \text{ C.} = 180° \text{ F.}; \text{ or } 5° \text{ C.} = 9° \text{ F.}$$

Consequently,

$$5 : 9 = 60 : 108.$$

But then, as Fahrenheit's scale commences with 32° instead of 0°, that number must be added to the result, making 60° C. = 140° F.

The rule, then, is the following:—To convert centigrade degrees into Fahrenheit degrees, multiply by 9, divide the product by 5, and add 32; to convert Fahrenheit degrees into centigrade degrees, subtract 32, multiply by 5, and divide by 9.

The reduction of negative degrees, or those below zero of one scale into those of another scale, is effected in the same way. For example, to convert −15° C. into degrees of Fahrenheit, we have—

$$-15 \times \frac{9}{5} + 32 = -27 + 32 = +5 \text{ F.}$$

In this work temperatures will always be given in centigrade degrees, unless the contrary is stated.

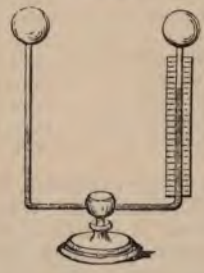
Mercury is usually chosen for making thermometers, on account of its regularity of expansion within certain limits, and because it is easy to have the scale of great extent, from the large interval between the freezing and boiling points of the metal. Other substances are sometimes used; alcohol is employed for estimating

very low temperatures, because this liquid has not been frozen even at the lowest degree of cold which has been artificially produced.

Air-thermometers are also used for some few particular purposes; indeed, the first thermometer ever made was of this kind. There are two modifications of this instrument: in the first, the liquid into which the tube dips is open to the air; and in the second, shown in fig. 22, the atmosphere is completely excluded. The effects of expansion are in the one case complicated with those arising from changes of pressure, and in the other they cease to be visible at all when the *whole* instrument is subjected to alterations of temperature, because the air in the upper and lower reservoir,

Fig. 22.

Fig. 23.



being equally affected by such changes, no alteration in the height of the fluid column can occur. Accordingly, such instruments are called *differential* thermometers, since they serve to measure differences of temperature between the two portions of air, while changes affecting both alike are not indicated. Fig. 23 shows another form of the same instrument.

The air-thermometer may be employed for measuring all temperatures from the lowest to the highest; Pouillet described one by which the heat of an air-furnace could be measured. The reservoir of this instrument is of platinum, and it is connected with a piece of apparatus by which the increase of volume experienced by the included air is determined.

An excellent air-thermometer has been constructed and used by Rudberg, and more recently by Magnus and Regnault, for measuring the expansion of the air. Its construction depends on the law, that when air is heated and hindered from expanding, its tension increases in the same proportion in which it would have increased in volume if permitted to expand.

All bodies are enlarged by the application of heat, and reduced

by its abstraction, or, in other words, contract on being artificially cooled: this effect takes place to a comparatively small extent with solids, to a larger amount in liquids, and most of all in the case of gases.

Each solid and liquid has a rate of expansion peculiar to itself; gases, on the contrary, expand nearly alike for the same increase of heat.

Expansion of Solids.—The actual amount of expansion which different solids undergo by the same increase of heat has been carefully investigated. The following are some of the results of the best investigations, more particularly those of Lavoisier and Laplace. The fraction indicates the amount of expansion in length suffered by rods of the undermentioned bodies in passing from 0° to 100°:—

Fir-wood*	$\frac{1}{2181}$	Tempered steel	$\frac{1}{807}$
English flint glass	$\frac{1}{1248}$	Soft iron	$\frac{1}{819}$
Platinum	$\frac{1}{1167}$	Gold	$\frac{1}{682}$
Common white glass	$\frac{1}{1100}$	Copper	$\frac{1}{584}$
Common white glass	$\frac{1}{1147}$	Brass	$\frac{1}{535}$
Glass without lead	$\frac{1}{1142}$	Silver	$\frac{1}{524}$
Another specimen	$\frac{1}{1000}$	Lead	$\frac{1}{351}$
Steel untempered	$\frac{1}{927}$	Zinc	$\frac{1}{333}$

From the *linear* expansion, the *cubic* expansion (or measure of volume) may be calculated. When the expansion of a body in different directions is equal, as, for example, in glass, hammered metals, and generally in most uncrystallised substances, it will be sufficient as an approximation to triple the fraction expressing the increase in one dimension. This rule does not hold true for crystals belonging to irregular systems, for they expand unequally in the direction of the different axes.

Metals appear to expand pretty uniformly for equal increments of heat within the limits stated; but above the boiling point of water the rate of expansion becomes irregular and more rapid.

The force exerted in the act of expansion is very great. In laying down railways, building iron bridges, erecting long ranges of steam-pipes, and in executing all works of the kind in which metal is largely used, it is indispensable to make provision for these changes of dimensions.

In consequence of glass and platinum having nearly the same amount of expansion, a thin platinum wire may be fused into a glass tube, without any fear that the glass will break on cooling.

A very useful application of expansion by heat, constantly practised in the laboratory for a great variety of purposes—is that of the cutting of glass by a hot iron. The glass to be cut is

* In the direction of the vessels.

marked with ink in the required direction, and then a crack, commenced by any convenient method, at some distance from the desired line of fracture, may be led by the point of a heated iron rod along the latter with the greatest precision.

Expansion of Liquids.—The dilatation of a liquid may be determined by filling a thermometer with it, in which the relation between the capacity of the ball and that of the stem is exactly known, and observing the height of the column at different temperatures. It is necessary in these experiments to take into account the effects of the expansion of the glass itself, the observed result being evidently the *difference* of the two.

Liquids vary exceedingly in this particular. The following table is taken from Péclet's "Éléments de Physique:"—

Apparent Dilatation in Glass between 0° and 100°.

Water	$\frac{1}{22}$
Hydrochloric acid, sp. gr. 1·137	$\frac{1}{27}$
Nitric acid, sp. gr. 1·4	$\frac{1}{9}$
Sulphuric acid, sp. gr. 1·85	$\frac{1}{17}$
Ether	$\frac{1}{14}$
Olive oil	$\frac{1}{12}$
Alcohol	$\frac{1}{9}$
Mercury	$\frac{1}{54}$

Most of these numbers must be taken as representing only mean results; for there are but few liquids, which, like mercury, expand regularly between these temperatures. Even mercury above 100° shows an unequal and increasing expansion, if the temperature indicated by the air-thermometer be used for comparison. This is shown by the following abstract of a table given by Regnault:—

Reading of Air Thermometer.	Reading of Mercurial Thermometer.	Temperature deduced from the Absolute Expansion of Mercury.
0°	0°	0°
100°	100°	100°
200°	200°	202·78°
300°	301°	308·34°
350°	354°	362·16°

The absolute amount of expansion of mercury is, for many reasons, a point of great importance; it has been very carefully determined by a method independent of the expansion of the containing vessel. The apparatus employed for this purpose, first by Dulong and Petit, and later by Regnault, is shown in fig. 24, divested, however, of many of its subordinate parts. It consists of two upright glass tubes, connected at their bases by a horizontal tube of much smaller dimensions. Since a free communication exists between the two tubes, mercury poured into the one will rise to the same level in

Expansion of Gases.—The principal laws relating to the expansion of gases are contained in the four following propositions :—

1. All gases expand nearly alike for equal increments of heat; and all vapours, when remote from their condensing points, follow the same law.
2. The rate of expansion is not altered by a change in the state of compression, or elastic force, of the gas itself.
3. The rate of expansion is uniform for all degrees of heat.
4. The actual amount of expansion is equal to $\frac{1}{273}$ or $\frac{11}{3000}$ or 0·003666 of the volume of the gas at 0° centigrade, for each degree of the same scale.*

It will not be necessary to enter into any description of the methods of investigation by which these results have been obtained; the advanced student will find in Pouillet's "Éléments de Physique," and in the papers of Magnus and Regnault,† all the information he may require.

In the practical manipulation of gases, it very often becomes necessary to make a correction for temperature, or to discover how much the volume of a gas would be increased or diminished by a particular change of temperature; this can be effected with great facility. Let it be required, for example, to find the volume which 100 cubic inches of any gas at 10° would assume on the temperature rising to 20°.

The rate of expansion is $\frac{1}{273}$ or $\frac{11}{3000}$ of the volume at 0° for each degree; or 3000 measures at 0° become 3011 at 1°, 3022 at 2°, 3110 at 10°, and 3220 at 20°. Hence

Meas. at 10°.		Meas. at 20°.		Meas. at 10°.		Meas. at 20°.
3110	:	3220	=	100	:	103·537

If this calculation is required to be made on the Fahrenheit scale, it must be remembered that the zero of that scale is 32° below the melting-point of ice. Above this temperature the expansion for each degree of the Fahrenheit scale is $\frac{1}{460}$ of the original volume.

This, and the correction for pressure, are operations of very frequent occurrence in chemical investigations, and the student will do well to become familiar with them.

The following formula includes both these corrections :—Let V and V′ be the volume of a gas at the temperatures t and t' centigrade, and under the pressures p and p', measured in millimeters of mercury : then

$$\frac{V}{V'} = \frac{1 + 0{\cdot}003666t}{1 + 0{\cdot}003666t'} \cdot \frac{p'}{p}$$

---

* The fraction $\frac{11}{3000}$ is very convenient for calculation.

† Poggendorff's Annalen, iv. 1—Ann. Chim. Phys. 3d series, iv. 5, and v. 52. See also Watts's Dictionary of Chemistry, art. Heat, vol. iii. p. 46; and Ganot's Éléments de Physique, translated by Dr. Atkinson, 4th edition, pp. 253—262.

The case which most frequently occurs is the reduction of a measured volume, V, of a gas at the temperature t and pressure p to the volume V_0, which it would occupy at 0° C., and under a pressure of 760 mm. In this case, we have $t' = 0$, and $p' = 760$, therefore

$$\frac{V}{V_0} = (1 + 0{\cdot}003666t) \cdot \frac{760}{p},$$

and

$$V_0 = \frac{V}{1 + 0{\cdot}003666t} \cdot \frac{p}{760}.$$

If the barometric pressure is measured in inches, the number 30 must be substituted for 760.

Note.—Of the four propositions stated in the text, the first and second have recently been shown to be true within certain limits only; and the third, although in the highest degree probable, would be very difficult to demonstrate rigidly; in fact, the equal rate of expansion of air is assumed in all experiments on other substances, and becomes the standard by which the results are measured.

The rate of expansion for the different gases is *not* absolutely the same, but the difference is so small that for most purposes it may safely be neglected. Neither is the state of elasticity altogether indifferent, the expansion being sensibly *greater* for an equal rise of temperature when the gas is in a compressed state.

It is important to notice that the greatest deviations from the rule are exhibited by those gases which, as will hereafter be seen, are most easily liquefied, such as carbon dioxide, cyanogen, and sulphur dioxide; and that the discrepancies become smaller and smaller as the elastic force is lessened; so that, if means existed for comparing the different gases in states *equally distant* from their points of condensation, there is reason to believe that the law would be strictly fulfilled.

The experiments of Dalton and Gay-Lussac gave for the rate of expansion $\frac{1}{201}$ of the volume at 0°: this is, no doubt, too high. Those of Rudberg give $\frac{1}{274}$, those of Magnus and of Regnault $\frac{1}{273}$.

Conduction of Heat.

Different bodies possess very different conducting powers with respect to heat: if two similar rods, the one of iron, the other of glass, be held in the flame of a spirit-lamp, the iron will soon become too hot to be touched, while the glass may be grasped with impunity within an inch of the red-hot portion.

Experiments made by analogous but more accurate methods have established a numerical comparison of the conducting powers of many bodies. The following may be taken as a specimen:—

Silver . .	1000	Steel . . .	116
Copper . .	736	Lead . . .	85
Gold . . .	532	Platinum . .	84
Brass . . .	236	German silver .	63
Tin . . .	145	Bismuth . .	18
Iron . . .	119		

As a class the metals are by very far the best conductors, although much difference exists between them ; stones, dense woods, and charcoal follow next in order ; then liquids in general, and lastly gases, whose conducting power is almost inappreciable.

Under favourable circumstances, nevertheless, both liquids and gases may become rapidly heated ; heat applied to the bottom of the containing vessel is very speedily communicated to its contents; this, however, is not so much by conduction, as by convection, or carrying. A complete circulation is set up ; the portions in contact with the bottom of the vessel get heated, become lighter, and rise to the surface, and in this way the heat becomes communicated to the whole. If these movements be prevented by dividing the vessel into a great number of compartments, the really low conducting power of the substance is made evident ; and this is the reason why certain organic fabrics, as wool, silk, feathers, and porous bodies in general, the cavities of which are full of air, exhibit such feeble powers of conduction.

The circulation of heated water through pipes is now extensively applied to the warming of buildings and conservatories ; and in chemical works a serpentine metal tube containing hot oil is often used for heating stills and evaporating pans ; the two extremities of the tube are connected with the ends of another spiral built into a small furnace at a lower level, and an unintermitting circulation of the liquid takes place as long as heat is applied.

Specific Heat.

Equal weights of different substances having the same temperature require different amounts of heat to raise them to a given degree of temperature. If 1 lb. of water, at 100°, be mixed with 1 lb. at 40°, then, as is well known, a mean temperature of $\frac{100+40}{2} = 70°$ is obtained. In the same way the mean temperature is found when warm and cold oil, or warm and cold mercury, &c., are mixed together. But if 1 lb. of water at 100° be shaken with 1 lb. of olive oil at 40°, or with 1 lb. of mercury at 40°, then, instead of the mean temperature of 70°, the temperature actually obtained will be 80° in the first case, 98° in the second ; 20 degrees of heat, which the water (by cooling from 100° to 80°) gave to the same weight of oil, were sufficient to raise the oil 40°, that is, from 40° to 80° ; and 2°, which the water lost by cooling from 100° to 98°, sufficed to heat an equal quantity of mercury 58°, namely from 40° to 98°.

It is evident from these experiments that the quantities of heat which equal weights of water, olive oil, and mercury, require to raise their temperature to the same height, are unequal, and that they are in the proportion of the numbers $1 : \frac{20}{40} : \frac{3}{58}$, or $1 : \frac{1}{2} : \frac{1}{29}$.

These quantities of heat, expressed relatively to the quantity of heat required to raise the temperature of an equal weight of water from 0° to 1° C., are called the specific heats of the various substances: thus the experiments just described show that the specific heat of olive oil is $\frac{1}{2}$, that is to say, the quantity of heat which would raise the temperature of any given quantity of olive oil from 0° to 1° would raise that of an equal weight of water only from 0° to $\frac{1}{2}$°, or of half that quantity of water from 0° to 1°.

The specific heats of bodies are sometimes said to measure their relative capacities for heat.

There are three distinct methods by which the specific heats of various substances may be estimated. The first of these is by observing the quantity of ice melted by a given weight of the substance heated to a particular temperature; the second is by noting the time which the heated body requires to cool down through a certain number of degrees; and the third is the method of mixture, on the principle illustrated; this last method is preferred as the most accurate.

The determination of the specific heat of different substances has occupied the attention of many experimenters; among these Dulong and Petit, and recently Regnault and Kopp, deserve especial mention.

From the observations of these and other physicists, it follows that each body has its peculiar specific heat, and that the specific heat increases with increase of temperature. If, for example, the heat which the unit of water loses by cooling from 10° to 0° be marked at 10°, then the loss by cooling from 50° to 0° will be, not 50, corresponding to the difference of temperature, but 50·1. By cooling from 100° to 0° it is 100·5, and rises to 203·2 when the water is heated under great pressure to 200°, and afterwards cooled to 0°. Similar and even more striking differences have been found with other substances. It has also been proved that the specific heat of any substance is greater in the liquid than in the solid state. For example, the specific heat of ice is 0·504, that is, not more than half as great as that of liquid water.

It is remarkable that the specific heat of water is greater than that of all other solid and liquid substances, and is exceeded only by that of hydrogen. The specific heat of the solid parts of the crust of the globe is on an average $\frac{1}{4}$, and that of the atmosphere nearly $\frac{1}{4}$ that of water.

If the specific heat of any body within certain degrees of temperature be accurately known, then from the quantity of heat which this body gives out when quickly dipped into cold water, the temperature to which the body was heated may be determined. Pouillet founded on this fact a method of measuring high temperatures,

and for this purpose, with the help of the air-thermometer, he determined the specific heat of platinum up to 1600°.

The determination of the specific heat of gases is attended with peculiar difficulties, on account of the comparatively large volume of small weights of gases. For many gases, however, satisfactory results have been obtained by the method of mixing.

When a gas expands, heat becomes latent, that is to say, insensible to the thermometer; in fact, the molecular motion which constitutes heat is converted into another kind of motion which overcomes the pressure to which the gas is subjected, and allows it to expand (see page 78). The amount of heat required, therefore, to raise a gas to any given temperature increases the more the gas in question is allowed to expand. The quantity of heat which the unit-weight of a gas requires in order to raise its temperature 1° without its volume undergoing any change (which can take place only by the pressure being simultaneously augmented) is called the specific heat of the gas *at constant volume*. The quantity of heat required by the unit-weight of a gas to raise its temperature 1°, it being at the same time allowed to dilate to such an extent that the pressure to which it is exposed remains unchanged, is called the specific heat of the gas *at constant pressure*. According to what has already been stated, the specific heat at constant pressure must be greater than that at constant volume. Dulong found, in the case of atmospheric air, of oxygen, of hydrogen, and of nitrogen, that the two specific heats are in the proportion 1·421 : 1. For carbon monoxide, however, he obtained the proportion of 1·423, for carbon dioxide 1·337, for nitrogen dioxide 1·343, and for olefiant gas 1·24 to 1. The exact determination of these ratios is extremely difficult, and the results of different physicists by no means agree.

The first satisfactory comparison of the specific heat of air with that of water was made by Count Rumford; later comparisons of the specific heat of various gases have been made by Delaroche and Bérard, Dulong and Regnault.

The first researches of Delaroche and Bérard furnished the results embodied in the following table :—

	Equal volumes.		Equal weights.	
	The volumes constant.	The pressure constant.	Air = 1.	Water = 1.
Atmospheric air	1	1	1	0·2669
Oxygen	1	1	0·9045	0·2414
Hydrogen	1	1	14·4510	3·8569
Nitrogen	1	1	1·0295	0·2748
Carbon monoxide	1	1	1·0337	0·2759
Nitrogen monoxide	1·227	1·160	0·7607	0·2030
Carbon dioxide	1·249	1·175	0·7685	0·2051
Olefiant gas	1·754	1·531	1·5829	0·4225

The latest and most trustworthy determinations are those of Regnault, given in the subjoined table, in the second column of

which the specific heats of the several gases and vapours are compared with that of an equal weight of water taken as unity, and in the third, with that of an equal volume of air referred to its own weight of water as unity. The latter series of numbers is obtained by multiplying the numbers in the second column by the specific gravities of the respective gases and vapours referred to air as unity :—

Gases.	*Specific Gravity.* Air = 1.	*Specific Heat at Constant Pressure.* For equal weights. Water = 1.	For equal volumes.
Atmospheric air	1	0·2377	0·2377
Oxygen	1·1056	0·2175	0·2405
Nitrogen	0·9713	0·2438	0·2368
Hydrogen	0·0692	3·4090	0·2359
Chlorine	2·4502	0·1210	0·2965
Bromine vapour	5·4772	0·0555	0·3040
Carbon monoxide	0·9670	0·2450	0·2370
Carbon dioxide	1·5210	0·2169	0·3307
Nitrogen monoxide	1·5241	0·2262	0·3447
Nitrogen dioxide.	1·0384	0·2317	0·2406
Olefiant gas	0·9672	0·4040	0·4106
Marsh gas	0·5527	0·5929	0·3277
Aqueous vapour	0·6220	0·4805	0·2989
Sulphuretted hydrogen	1·1746	0·2432	0·2857
Sulphur dioxide	2·2112	0·1544	0·3414
Vapour of carbon bisulphide	2·6258	0·1569	0·4122
Hydrochloric acid	1·2596	0·1852	0·2333
Ammonia	0·5894	0·5084	0·2996

The researches of Delaroche and Bérard led them to suppose that the specific heat of gases increased rapidly as the temperature was raised, and that for a given volume of gas it increased in proportion to the density or tension of the gas. Regnault found, however, the quantity of heat which a given volume of gas requires to raise it to a certain temperature, to be independent of its density ; and that for each degree between −30° and 225° it is constant. Carbon dioxide, however, forms an exception to this rule, its specific heat increasing with the temperature. In the table mean values for temperatures between 10° and 200° have been given.

Several physicists have held that the specific heats of elementary gases, referred to equal volumes, are identical. The numbers which Regnault found for chlorine and bromine, however, show that the law does not hold good for all elementary gases.

It has been already stated that, when a gas expands, heat becomes latent. If a gas on expanding be not supplied with the requisite heat, its temperature will fall, on account of its own free heat becoming latent, that is to say, expended in overcoming pressure. On the other hand, if a gas be compressed, this latent heat becomes free,

a known weight of water of known temperature, the rise in temperature of the water being then noted, the temperature at which the fusion occurred may be found from the equation—

$$T = \theta + \frac{(W + w)\, r\, (\theta - t)}{Ms},$$

in which W denotes the weight of water in the calorimeter ; w the thermal value of the calorimeter + mercury and glass of thermometer in grams of water ; M the weight of the crucible ; r the specific heat of water ; s the specific heat of platinum (from 0° to T) ; t the initial, and θ the final temperature of the water. Solidifying points may be determined in a similar manner, but with this difference, that when the salt has completely melted, the lamp is turned out, and the crucible dropped into the calorimeter at the instant when the salt begins to solidify.

The following table exhibits the melting and solidifying points of several salts determined in this manner :—

	M. P.	S. P.	Difference.
Potassium nitrate . . .	353°	332°	21
„ chlorate . . .	372	351	21
„ chloride . . .	434	415	19
„ iodide . . .	639	622	17
„ bromide . . .	703	685	18
„ carbonate . . .	838	832	6

Latent Heat of Fusion.—During fusion bodies absorb a certain quantity of heat which is not indicated by the thermometer.

If equal weights of water at 0° and water at 79° be mixed, the temperature of the mixture will be the mean of the two temperatures, viz., 39·5° ; but if the same experiment be made with snow or finely powdered ice at 0° and water at 79°, the temperature of the mixture will be only 0°, *but the ice will have been melted.*

1 lb. of water at 0° } = 2 lb. water at 39·5°.
1 lb. of water at 79° }

1 lb. of ice at 0° } = 2 lb. water at 0°.
1 lb. of water at 79° }

In the last experiment therefore, as much heat has been apparently lost as would have raised a quantity of water equal to that of the ice through a range of 79 degrees.

The heat, thus become insensible to the thermometer in effecting the liquefaction of the ice, is called latent heat, or better, heat of fluidity.

Again, let a perfectly uniform source of heat be imagined, of such intensity that a pound of water placed over it would have its temperature raised 5° per minute. Starting with water at 0°, in rather less than 16 minutes its temperature would have risen 79° ; but the same quantity of ice at 0°, exposed for the same interval of time,

would not have its temperature raised a single degree. But, then, it would have become water, the heat received being exclusively employed in effecting the change of state.

This heat is not lost, for when the water freezes it is again evolved. If a tall jar of water, covered to exclude dust, be placed in a situation where it shall be quite undisturbed, and at the same time exposed to great cold, the temperature of the water may be reduced 5° or more below its freezing point without the formation of ice; * but, if a little agitation be then communicated to the jar, or a grain of sand dropped into the water, a portion instantly solidifies, and the temperature of the whole rises to 0°; the heat disengaged by the freezing of a small portion of the water is sufficient to raise the whole contents of the jar 5°.

This condition of instable equilibrium shown by the very cold water in the preceding experiment, may be reproduced with a variety of solutions which tend to crystallise or solidify, but in which that change is for a while suspended. Thus, a solution of crystallised sodium sulphate in its own weight of warm water, left to cool in an open vessel, deposits a large quantity of the salts in crystals. If, however, the warm solution be filtered into a clean flask, which when full is securely corked and set aside to cool undisturbed, no crystals will be deposited even after many days, until the cork is drawn and the contents of the flask are agitated. Crystallisation then rapidly takes place in a very beautiful manner, and the whole becomes perceptibly warm.

The law above illustrated in the case of water is perfectly general. Whenever a solid becomes a liquid, a certain fixed and definite amount of heat disappears, or becomes latent; and conversely, whenever a liquid becomes solid, heat to a corresponding extent is given out.

The following table exhibits the melting points of several substances, and their latent heats of fusion expressed in gram-degrees—that is to say, the numbers in the column headed "latent heat" denote the number of grams of water, the temperature of which would be raised 1° centigrade by the quantity of heat required to fuse one gram of the several solids :—

---

* Fused bodies, when cooled down to or below their fusing point, frequently remain liquid, more especially when not in contact with solid bodies. Thus, water in a mixture of oil of almonds and chloroform, of specific gravity equal to its own, remains liquid to −10°; in a similar manner fused sulphur or phosphorus, floating in a solution of zinc chloride of appropriate concentration, retains the liquid condition at temperatures 40° below its fusing point. Liquid bodies, thus cooled below their fusing point, frequently solidify when touched with a solid substance, invariably when brought in contact with a fragment of the same body in the solid state. A body thus retained in the liquid state above its ordinary solidifying point, is said to be in a state of *surfusion* or *superfusion*.

E.

Substance.	Melting Point.	Latent Heat.	Substance.	Melting Point.	Latent Heat.
Mercury . .	−39°	2·82	Tin . . .	235°	14·25
Phosphorus . .	+44	5·0	Silver . . .	1000	21·1
Lead . . .	332	5·4	Zinc . . .	433	28·1
Sulphur . . .	115	9·4	Calcium chloride ($CaCl_2,6H_2O$)	28·5	40·7
Iodine . . .	107	11·7			
Bismuth . .	270	12·6	Potassium nitrate .	339	47·4
Cadmium . .	320	13·6	Sodium nitrate .	310·5	63·0

Freezing Mixtures.—When a solid substance can be made to liquefy by a weak chemical attraction, cold results, from sensible heat becoming latent. This is the principle of frigorific mixtures. When snow or powdered ice is mixed with common salt, and a thermometer plunged into the mass, the mercury sinks to 0° F. (− 17·7° C.), while the whole after a short time becomes fluid; such a mixture is very often used in chemical experiments to cool receivers and condense the vapours of volatile liquids. Powdered crystallised calcium chloride and snow produce cold enough to freeze mercury. Even powdered potassium nitrate, or sal-ammoniac, or ammonium nitrate, dissolved in water, occasions a very notable depression of temperature; in every case, in short, in which solution is unaccompanied by energetic chemical action, cold is produced.

No relation can be traced between the actual melting point of a substance and its latent heat when in the fused state.

2. *Vaporisation and Condensation.*

A law of exactly the same kind as that above described affects universally the gaseous condition; change of state from solid or liquid to gas is accompanied by absorption of sensible heat, and the reverse by its disengagement. The latent heat of steam and other vapours may be ascertained by a mode of investigation similar to that employed in the case of water.

When water at 0° is mixed with an equal weight of water at 100°, the whole is found to have the mean of the two temperatures, or 50°; on the other hand, 1 part by weight of *steam* at 100°, when condensed in cold water, is found to be capable of raising 5·4 parts of the latter from the freezing to the boiling point, or through a range of 100°. Now $100 \times 5{\cdot}4 = 540°$; that is to say, steam at 100°, in becoming water at 100°, parts with enough heat to raise a weight of water equal to its own (if it were possible) 540° of the thermometer, or 540 times its own weight of water one degree. When water passes into steam the same quantity of sensible heat becomes latent.

The vapours of other liquids seem to have less latent heat than that of water. The following table, drawn up by Dr. Andrews of Belfast, serves well to illustrate this point. The latent heats are expressed, as in the last table, in gram-degrees :—

	Latent Heat.
Vapour of water	535·90°
„ alcohol	202·40
„ ether	90·45
„ ethyl oxalate	72·72
„ „ acetate	92·68
„ „ iodide	46·87
„ methyl alcohol	263·70
„ carbon bisulphide	86·67
„ tin tetrachloride	30·35
„ bromine	45·66
„ oil of turpentine	74·03

Boiling or Ebullition is occasioned by the formation of bubbles of vapour within the body of the evaporating liquid, which rise to the surface like bubbles of permanent gas. This occurs in different liquids at very different temperatures. Under the same circumstances, the boiling point is quite constant, and often becomes a physical character of great importance in distinguishing liquids which much resemble each other. A few cases may be cited in illustration :—

Substance.	Boiling Point.
Aldehyde	22°
Ether	35·6
Carbon bisulphide	46·1
Alcohol	78·4
Water	100
Nitric acid (sp. gr. 1·414 at 15·5°)	120·5
Oil of turpentine	157
Sulphuric acid	338
Mercury	357

For ebullition to take place, it is necessary that the elasticity of the vapour should be able to overcome the cohesion of the liquid and the pressure upon its surface ; hence the extent to which the boiling point may be modified.

Water, under the usual pressure of the atmosphere, boils at 100° C. (212° F.); in a partially exhausted receiver or on a mountain-top it boils at a much lower temperature ; and in the best vacuum of an air-pump, over oil of vitriol, which absorbs the vapour, it will often enter into violent ebullition while ice is in the act of forming upon the surface.

On the other hand, water confined in a very strong metallic vessel may be restrained from boiling by the pressure of its own vapour to an almost unlimited extent; a temperature of 177° or 204°

sary to raise a unit-weight of water from 0° to $t°$ is not exactly denoted by t; the discrepancy, however, is so small that it may be disregarded. Employing the approximate value, the latent heat of steam, L, at any temperature will be found by subtracting t from the total heat; or, according to the formula :—

$$L = 606{\cdot}5 - 0{\cdot}695t.$$

This equation shows us the remarkable fact that the latent heat of steam diminishes as the temperatures rises. Before Regnault's experiments were made, two laws of great simplicity were generally admitted, one of which, however, contradicted the other. Watt concluded, from experiments of his own, as well as from theoretical speculations, that the total heat of steam would be the same at all temperatures. Were this true, equal weights of steam passed into cold water would always exhibit the same heating power, no matter what the temperature of the steam might be. Exactly the same *absolute* amount of heat, and consequently the same quantity of fuel, would be required to evaporate a given weight of water *in vacuo* at a temperature which the hand can bear, or under great pressure and at high temperature. Watt's law, though agreeing well with the rough practical results obtained by engineers, is only approximately true; and the same may be said of the deductions which have just been made from it. The second law, in opposition to Watt's is that of Southern, stating the latent heat of steam to be

Fig. 26.

the same at all temperatures. Regnault's researches have shown that neither Watt's law (T constant) nor Southern's law (L constant) is correct.

Distillation.—The process of distillation is very simple: its object is either to separate substances which rise in vapour at different

atmospheres—at which point the difficulties and danger became so great as to put a stop to the inquiry; the rest of the table is the result of calculations founded on the data so obtained :—

Pressure of Steam in Atmospheres.	Corresponding Temperature.	Pressure of Steam in Atmospheres	Corresponding Temperature.
1	100°	13	194°
1·5	112	14	197
2	122	15	200·5
2·5	129	16	203
3	135	17	207
3·5	140·5	18	209
4	145·5	19	212
4·5	149	20	214
5	153	21	217
5·5	157	22	219
6	160	23	222
6·5	163	24	224
7	167	25	226
7·5	169	30	236
8	172	35	245
9	177	40	253
10	182	45	255
11	186	50	266
12	190		

It is very interesting to know the amount of heat requisite to convert water of any given temperature into steam of the same or another given temperature. The most exact experiments on this subject are due to Regnault. He arrived at this result, that when the unit-weight of steam at the temperature $t°$ is converted into water of the same temperature, and then cooled to 0°, it gives out a quantity of heat T, represented by the formula :—

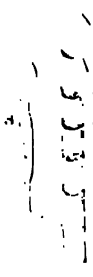
$$T = 606{\cdot}5 + 0{\cdot}305t.$$

This formula appears to hold good for temperatures both above and below the ordinary boiling point of water. The following table gives the values of T, corresponding to the respective temperatures in the first column :—

t.	T.
0°	606·5°
50	621·7
100	637·0
150	652·2
200	667·5

T is called the total heat of steam, being the heat required to raise water from 0° to $t°$, together with that which becomes latent by the transformation of water at $t°$ into steam at $t°$. Regnault states, as a result of some very delicate experiments, that the heat neces-

[illegible] while the intermediate fractions will [illegible] the original mixture, and must all [illegible] in order to obtain more complete [illegible] separations being generally long and [illegible] adopted for facilitating the [illegible] by causing the vapour of the less [illegible] constituent to condense in the upper [illegible] of the distilling apparatus, and run back [illegible] The way of effecting this partial con- [illegible] is to surmount the flask or other [illegible] with a vertical tube, having [illegible] bulbs blown on it, and a side- [illegible] for the passing into the condenser; [illegible] further separation may be effected [illegible] rings of platinum gauze *c c* in the [illegible] tube. The less volatile liquid then [illegible] in the meshes of these cups and [illegible] vapour in passing through them is washed, as it were, by this condensed liquid, a further portion of which is dissolved out of the vapour by the portion already condensed. A side-tube *s* may also be attached to one of the bulbs to facilitate this running back of the liquid into the flask.



In some cases, however, the separation of the mixed liquids cannot be effected by fractional distillation. Wanklyn* has shown that when a mixture of equal parts by weight of two liquids of different boiling point is distilled, the quantity of each constituent in the distillate is proportional to the product of its vapour-density and vapour tension at the boiling point of the fraction. Hence, if the vapour tensions and vapour-densities of the two liquids are proportional to one another, the mixture will distil unchanged. For example, a mixture of 91 parts carbon bisulphide (b. p. 46°) and 9 parts ethyl alcohol (78·4°), distils without alteration at 43° to 44°; and a mixture of equal volumes of carbon tetrachloride (b. p. 76·6°) and methyl alcohol (b. p. 65·2°) distils unaltered at 55·6° to 59°, that is to say, nearly 10° lower than the boiling point of the more volatile constituent.

Tension of Vapours. Liquids evaporate at temperatures below their boiling points; in this case the evaporation takes place slowly from the surface. Water, or alcohol, exposed in an open vessel at the temperature of the air, gradually disappears; the more rapidly, the warmer and drier the air.

This fact was formerly explained by supposing that air and gases in general had the power of dissolving and holding in solution certain quantities of liquids, and that this power increased with the temperature. Such an idea is incorrect.

* Phil. Mag. [4], xiv. p. 139.

If a barometer-tube be carefully filled with mercury and inverted in the usual manner, and then a few drops of water passed up the tube into the vacuum above, a very remarkable effect will be observed,—the mercury will be depressed to a small extent, and this depression will increase with increase of temperature. Now, as the space above the mercury is void of air, and the weight of the few drops of water quite inadequate to account for this depression, it must of necessity be imputed to the vapour which instantaneously rises from the water into the vacuum; and that this effect is really due to the elasticity of the aqueous vapour, is easily proved by exposing the barometer to a heat of 100°, when the depression of the mercury will be complete, and it will stand at the same level within and without the tube; indicating that at that temperature the elasticity of the vapour is equal to that of the atmosphere—a fact which the phenomenon of ebullition has already shown.

By placing over the barometer a wide open tube dipping into the mercury below (fig. 29), and then filling this tube with water at different temperatures, the tension of the aqueous vapour for each degree of the thermometer may be accurately determined by its depressing effect upon the mercurial column; the same power which forces the latter *down* one inch against the pressure of the atmosphere, would of course *elevate* a column of mercury to the same height against a vacuum, and in this way the tension may be conveniently expressed. The following table was drawn up by Dalton, to whom we owe this method of investigation :—

Fig. 29.

Temperature. F.	Temperature. C.	Tension in Inches of Mercury.	Temperature. F.	Temperature. C.	Tension in Inches of Mercury.
32°	0°	0·200	130°	54·4°	4·34
40	4·4	0·263	140	60	5·74
50	10	0·375	150	65·5	7·42
60	15·5	0·524	160	71·1	9·46
70	21·1	0·721	170	76·6	12·13
80	26·6	1·000	180	82·2	15·15
90	32·2	1·360	190	87·7	19·00
100	37·7	1·860	200	93·3	23·64
110	43·3	2·530	212	100	30·00
120	48·8	3·330			

Another table representing the tension of the vapour of water, drawn up by Regnault, is given in the Appendix to this volume.

Other liquids tried in this manner are found to emit vapours of greater or less tension, for the same temperature, according to their different degrees of volatility; thus, a little ether introduced into the tube depresses the mercury 10 inches or more at the ordi-

nary temperature of the air; oil of vitriol, on the other hand, does not emit any sensible quantity of vapour until a much greater heat is applied; and that given off by mercury itself in warm summer weather, although it may be detected by very delicate means, is far too small to exercise any effect upon the barometer. In the case of water, the evaporation is quite distinct and perceptible at the lowest temperatures when the water is frozen to solid ice in the barometer-tube; snow on the ground, or on a housetop, may often be noticed to vanish, from the same cause, day by day in the depth of winter, when melting is impossible.

There exists for each vapour a state of density which it cannot pass without losing its gaseous condition, and becoming liquid; this is called the *condition of maximum density*. When a volatile liquid is introduced in sufficient quantity into a vacuum, this condition is always reached, and then evaporation ceases. Any attempt to increase the density of this vapour by compressing it into a smaller space will be attended by the liquefaction of a portion, the density of the remainder being unchanged. If a little ether be introduced into a barometer-tube, and the latter slowly sunk into a very deep cistern of mercury (fig. 30) it will be found that the height of the column of mercury in the tube above that in the cistern remains unaltered until the upper extremity of the tube approaches the surface of the metal in the column, and all the ether has become liquid. It will be observed also, that, as the tube sinks, the stratum of liquid ether increases in thickness, but no increase of elastic force occurs in the vapour above it, and consequently, no increase of density: for tension and density are always, under ordinary circumstances at least, directly proportionate to each other.

Fig. 30.

The maximum density of vapours is dependent upon the temperature; it increases rapidly as the temperatures rises. This is well shown in the case of water. Thus, taking the specific gravity of atmospheric air at 100° = 1000, that of aqueous vapour in its greatest state of compression for the temperature will be as follows:—

Temperature. F.	Temperature. C.	Specific Gravity.	Weight of 100 Cubic Inches.
32°	0°	5·690	0·136 grains.
50	10	10·293	0·247 „
60	15·5	14·108	0·338 „
100	37·7	46·500	1·113 „
150	65·5	170·293	4·076 „
212	100	625·000	14·962 „

The last number was experimentally found by Gay-Lussac; the others are calculated from it by the aid of Dalton's table of tensions, on the assumption that steam, not in a state of saturation, that is, below the point of greatest density, obeys Boyle's law (which is, however, only approximately true), and that when it is cooled it contracts like the permanent gases.

Thus, there are two distinct methods by which a vapour may be reduced to the liquid form—*pressure*, by causing increase of density until the point of maximum density for a given temperature is reached: and *cold*, by which the point of maximum density is itself lowered. The most powerful effects are produced when the two are conjoined.

For example, if 100 cubic inches of vapour of water at 100° F., in the state above described, had its temperature reduced to 50° F., not less than 0·89* grain of liquid water would necessarily separate, or very nearly eight-tenths of the whole.

Evaporation into a space filled with air or gas follows the same law as evaporation into a vacuum; as much vapour rises and the condition of maximum density is assumed in the same manner as if the space were perfectly empty; the sole difference lies in the length of time required. When a liquid evaporates into a vacuum, the point of greatest density is attained at once, while in the other case some time elapses before this happens: the particles of air appear to oppose a sort of mechanical resistance to the rise of the vapour. The ultimate effect is, however, precisely the same.

When to a quantity of perfectly dried gas confined in a vessel closed by mercury, a little water is added, the latter immediately begins to evaporate, and after some time as much vapour will be found to have risen from it as if no gas had been present, the quantity depending entirely on the temperature to which the whole is subjected. The tension of this vapour will add itself to that of the gas, and produce an expansion of volume, which will be indicated by an alteration of level in the mercury.

Vapour of water exists in the atmosphere at all times, and in all situations, and there plays a most impotant part in the economy of nature. The proportion of aqueous vapour present in the air is subject to great variation, and it often becomes important to determine its quantity. This is easily done by the aid of the foregoing principles.

Dew-point.—If the aqueous vapour be in its condition of greatest possible density for the temperature, or, as it is frequently but most incorrectly expressed, the air be saturated with vapour of water, the slightest reduction of temperature will cause the deposition of a portion in the liquid form. If, on the contrary, as is almost always in reality the case, the vapour of water is *below* its state of maximum

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* 100 cub. inch. aqueous vapour at 100° F., weighing 1·113 grains, would at 50° F. become reduced to 91·07 cub. inch., weighing 0·225 grain.

density, that is, in an expanded condition, it is clear that a considerable fall of temperature may occur before liquefaction commences. The degree at which this takes place is called the dew-point, and it is determined with great facility by a very simple method. A little cup of thin tin-plate or silver, well polished, is filled with water at the temperature of the air, and a delicate thermometer inserted. The water is then cooled by dropping in fragments of ice, or dissolving in it powdered sal-ammoniac until moisture begins to make its appearance on the outside, dimming the bright metallic surface. The temperature of the dew-point is then read off upon the thermometer, and compared with that of the air.

Suppose, by way of example, that the latter were 70° F., and the dew-point 50° F., the elasticity of the watery vapour present would correspond with a maximum density proper to 50° F., and would support a column of mercury 0·375 inch high. If the barometer on the spot stood at 30 inches, therefore, 29·625 inches would be supported by the pressure of the dry air, and the remaining 0·375 inch by the vapour. Now, a cubic foot of such a mixture must be looked upon as made up of a cubic foot of dry air, and a cubic foot of watery vapour, occupying the same space, and having tensions indicated by the numbers just mentioned. A cubic foot, or 1728 cubic inches of vapour at 70° F., would become reduced by contraction, according to the usual law, to 1662·8 cubic inches at 50° F.; this vapour would be at its maximum density, having the specific gravity pointed out in the table: hence 1662·8 cubic inches would weigh 4·11 grains. The weight of the aqueous vapour contained in a cubic foot of air will thus be ascertained. In this country the difference between the temperature of the air and the dew-point seldom reaches 30° F. (16·6° C.); but in the Deccan, with a temperature of 90° F. (32·2° C.), the dew-point sinks as low as 19° F., making the degree of dryness 61° F.*

Liquefaction and Solidification of Gases.—The perfect resemblance in every respect which vapours bear to permanent gases, led, very naturally, to the idea that the latter might, by the application of suitable means, be made to assume the liquid state, and this surmise has been verified. The first experiments in this direction were made by Faraday, who succeeded in liquefying eight gases previously regarded as permanent. The subjoined table shows the results of his first investigations, with the pressure in atmospheres, and the temperatures at which the condensation takes place.

* Daniell, Introduction to Chemical Philosophy, p. 154.

	Atmospheres.	Temperatures. F.	C.
Sulphur	2	45°	7·2°
Hydrogen sulphide	17	50	10
Carbon dioxide	36	32	0
Chlorine	4	60	15·5
Nitrogen monoxide	50	45	7·2
Cyanogen	3·6	45	7·2
Ammonia	6·5	50	10
Hydrochloric acid	40	50	10

The method of proceeding was very simple : the materials were sealed up in a strong narrow tube, together with a little pressure-gauge, consisting of a slender tube closed at one end, and having within it, near the open extremity, a globule of mercury. The gas being disengaged by heat, accumulated in the tube, and by its own pressure brought about condensation. The force required for this purpose was judged of by the diminution of volume of the air in the gauge.

Fig. 31.

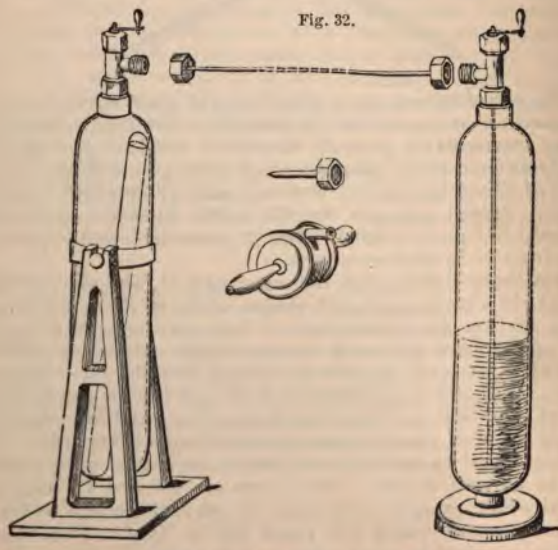
By the use of narrow green glass tubes of great strength, powerful condensing syringes, and an extremely low temperature, produced by means to be presently described, ethylene gas, hydriodic and hydrobromic acids, phosphoretted hydrogen, and the gaseous fluorides of silicon and boron, were successively liquefied. Oxygen, hydrogen, nitrogen, nitrogen dioxide, carbon monoxide, and marsh gas, refused to liquefy even at − 166° F. while subjected to pressures varying from 27 to 58 atmospheres.

Sir Isambard Brunel, and, more recently, M. Thilorier, of Paris, succeeded in obtaining liquid carbon dioxide (commonly called carbonic acid) in great abundance. Thilorier's apparatus (fig. 32) consists of a pair of extremely strong metallic vessels, one of which is destined to serve the purpose of a retort, and the other that of a receiver. They are made either of thick cast iron or gun metal, or, better, of the best and heaviest boiler-plate, and are furnished with stop-cocks of peculiar kind and excellent workmanship. The generating vessel or retort has a pair of trunnions upon which it swings in an iron frame. The joints are secured by collars of lead, and every precaution is taken to prevent leakage under the enormous pressure which the vessel has to bear. The receiver resembles the retort in every respect ; it has a similar stop-cock, and is connected with the retort by a strong copper tube and a pair of union screw-joints ; a tube passes from the stop-cock downwards, and terminates near the bottom of the vessel.

The operation is thus conducted: $2\frac{3}{4}$ lb. of acid sodium carbonate, and $6\frac{1}{4}$ lb. of water at 100° F., are introduced into the generator; oil of vitriol to the amount of $1\frac{1}{2}$ lb. is poured into a copper cylindrical vessel, which is lowered down into the mixture, and set upright; the stop-cock is then screwed into its place, and forced home by a spanner and mallet. The machine is next tilted up on its trunnions, that the acid may run out of the cylinder and mix with the other contents of the generator; and this mixture is favoured by swinging the whole backwards and forwards for a few minutes, after which it may be suffered to remain a little time at rest.

The receiver, surrounded with ice, is next connected with the generator, and both cocks are opened; the liquefied carbon dioxide distils over into the colder vessel, and there again in part condenses. The cocks are now closed, the vessel is disconnected, the cock of the generator opened to allow the contained gas to escape; and, lastly, when the issue of gas *has quite ceased*, the stop-cock itself is unscrewed, and the sodium sulphate turned out. This operation must be repeated five or six times before any considerable quantity of liquefied carbon dioxide will have accumulated in the receiver.

Fig. 32.



When the receiver thus charged has its stop-cock opened, a stream of the liquid is forcibly driven up the tube by the elasticity of the gas contained in the upper part of the vessel.

The experimenter incurs great personal danger in using this apparatus, unless the utmost care be taken in its management. A dreadful accident occurred in Paris by the bursting of one of the iron vessels.

Liquid carbon dioxide is also very frequently prepared by means of an apparatus constructed by Natterer, of Vienna, which enables the experimenter to work with less risk. The gas, disengaged by means of sulphuric acid from acid potassium carbonate, is pumped by means of a force-pump into a wrought-iron vessel, exactly as the air is pumped into the receiver of an air-gun. When a certain pressure has been reached, the gas is liquefied, and if the pressure be continued considerable quantities of the liquid carbon dioxide may be thus obtained. By this apparatus, nitrous oxide has been condensed to a liquid without the use of frigorific mixtures.

There still, however, remained six gases, viz., hydrogen, oxygen, nitrogen, nitrogen dioxide, carbon monoxide, and methane or marsh-gas, which down to the year 1877 had resisted all attempts to reduce them to the solid or liquid state ; but towards the end of that year they were all liquefied by Cailletet* and Pictet,† who employed methods exactly similar in principle to those used by Faraday, consisting in the application of cold and pressure, the gases being condensed in thick walled tubes of fine bore by means of forcing-pumps capable of producing a pressure of 300 to 1000 atmospheres, and at the same time subjected to the intense cold produced by a mixture of liquid sulphur dioxide and solid carbon dioxide.

Complete Vaporisation of Liquids under great Pressures.—When the temperature of a liquid is raised sufficiently high, vaporisation occurs under the highest pressure to which the substance can be subjected. Alcohol, ether, or rock-oil, enclosed in a tube of strong glass or iron, is completely converted into vapour, only when the space not occupied by the liquid is somewhat greater than the volume of the liquid itself. With rock-oil the empty space may be somewhat smaller than with alcohol, and with ether still less. Alcohol when thus heated acquires increased mobility, expands to twice its original volume, and is then suddenly converted into vapour. This change takes place at 207° C. (404·6° F.), when the alcohol occupies just half the volume of the tube ; if the tube is more than half filled with alcohol, it bursts when heated. A glass tube one-third filled with water becomes opaque when heated, and bursts after a few seconds. If the chemical action of the water on the glass be diminished by the addition of a little carbonate of soda, the transparency of the glass will be much less impaired ; and if the space occupied by the water be $\frac{1}{4}$ of the whole tube, the liquid will be converted into vapour at about the temperature of

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* Comptes rendus, lxxxv. pp. 1016, 1213, 1217, 1270.
† Ibid., lxxxv. pp. 1214, 1276 ; lxxxvi. pp. 37, 106.

melting zinc. These observations were made by Cagniard de Latour in 1822.

In like manner Dr. Andrews has observed that when liquid carbon dioxide is gradually heated in a sealed tube to 31°, the surface of demarcation between the liquid and gas becomes fainter, loses its curvature, and at last disappears. The space is then occupied by a homogeneous fluid, which exhibits, when the pressure is suddenly diminished, or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 31° no apparent liquefaction of carbon dioxide or separation into two distinct forms of matter can be effected, even under a pressure of 300 or 400 atmospheres. Similar results are obtained with nitrous oxide.

It appears indeed that there exists for every liquid a temperature, called by Andrews the "critical point," above which no amount of pressure is sufficient to retain it in the liquid form; it is therefore not surprising that mere pressure, however intense, should fail to liquefy many bodies which usually exist in the form of gas.

Under the enormous pressures to which gases can be thus subjected, without liquefaction, they are found to deviate greatly from the laws of Boyle and Gay-Lussac (pp. 28, 40). Andrews has recently found that carbon dioxide, at 60·7° under a pressure of 223 atmospheres, is reduced to $\frac{1}{147}$ of its original volume, or to less than one-half the volume it should occupy if it contracted according to Boyle's law. The co-efficient of expansion of the same gas by heat increases rapidly with the pressure; between 6° and 64° it is $1\frac{1}{2}$ times as great under 22 atmospheres, and more than $2\frac{1}{2}$ times as great at 40 atmospheres as at the pressure of 1 atmosphere.*

Cold produced by Evaporation.—This effect has been already adverted to: it arises from the conversion of sensible heat into latent by the rising vapour, and may be illustrated in a variety of ways. Ether dropped on the hand produces the sensation of great cold; and water contained in a thin glass tube, surrounded by a bit of rag, is speedily frozen when the rag is kept wetted with ether.

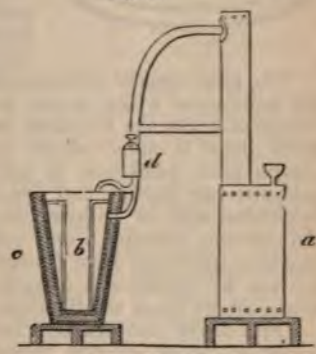
Ice-making machines and refrigerators are constructed on this principle. Harrison's apparatus for freezing water consists of a multitubular boiler containing about 10 gallons of ether and immersed in a trough of salt water. The boiler is connected with an exhausting pump, by the working of which the ether is rapidly volatilised, thereby cooling the boiler and the salt water surrounding it to about 24° F. (−4·45° C.) This cold water is made to flow through a channel in which are placed a number of vessels containing the water to be frozen, and when its temperature has been thus raised to about 28°, it is pumped back again into the trough con-

* Journal of the Chemical Society, 1876, vol ii. p. 162.

taining the boiler, and then again cooled by the evaporation of the ether. In this manner a constant supply of cold salt water is kept up. The ether which is evaporated is condensed in a worm surrounded by cold water, and returned with very little loss to the boiler.*

A simpler freezing apparatus is that of Carré, in which cold is produced by the rapid evaporation of liquefied ammonia-gas. It consists essentially of a cylindrical boiler *a*, fig. 33, holding about two gallons, filled to about three-fourths of its capacity with a strong aqueous solution of ammonia, and connected by pipes with a wrought-iron annular condenser or freezer *c*. The boiler is first placed in a furnace, and the freezer in water cooled to 12° C. (53·6° F.). The boiler is heated to 130° C., whereupon ammonia gas is given off, and condenses in the freezer, together with about one-tenth of its own weight of water. This operation being completed, the boiler is removed from the fire and immersed in cold water; the freezer, wrapped in very dry flannel, is placed outside, and the vessel containing the water to be frozen is placed in the cylindrical space *b*. As the boiler cools, the ammonia gas with which it is filled is redissolved, and the pressure being thus diminished, the ammonia which has been liquefied in *c* is again volatilised, and passes over towards *a*, to redissolve in the water which has remained in the boiler. This rapid evaporation of the ammonia causes a great absorption of heat, whereby the vessel *c* is reduced to a very low temperature, and the water contained in it is frozen. To obtain better contact between the sides of the vessel *b* and the freezer, alcohol is poured between them. This apparatus gives about 4 lb. of ice in an hour at the price of about a farthing a pound; but large continuously working apparatus have been constructed which produce as much as 800 lb. of ice in an hour.†

Fig. 33.



Another method of producing very low temperatures is by the rapid evaporation of methyl chloride, CH_3Cl, which is now prepared on the large scale from beetroot molasses (*see* vol. ii.). This compound is gaseous at ordinary temperatures and pressure, and when

* A figure of this apparatus is given in the Pharmaceutical Journal, vol. xvi. p. 477.

† See Richardson and Watts's Chemical Technology, part v. p. 296.

liquefied boils at − 23° ; and by blowing air through this liquid, or better by placing it in connection with a good air-pump, its temperature may in a very short time be reduced to − 55°. Powerful refrigerating machines are now constructed on this principle.

Water may also be frozen by the cold resulting from its own evaporation. When a little water is put into a watch-glass, supported by a triangle of wire over a shallow glass dish of sulphuric acid placed on the plate of an air-pump, the whole covered with a low receiver, and the air withdrawn as perfectly as possible, the water is in a few minutes converted into a solid mass of ice. The absence of the air, and the rapid absorption of watery vapour by the oil of vitriol, induce such quick evaporation that the water has its temperature almost immediately reduced to the freezing point.

Fig. 34.

The same apparatus is constantly used in the laboratory for drying substances which cannot bear heating without decomposition. Frequently also the air-pump is dispensed with, and the substance to be dried is simply placed over a vessel containing strong sulphuric acid, quicklime, or some other substance which absorbs moisture very rapidly, and covered over with a bell-jar. Such an apparatus, with or without the air-pump, is called an *Exsiccator*. On the same principle a very powerful ice-making and refrigerating machine has lately been constructed, by which large quantities of ice can be rapidly and economically produced without the use of ether, or any other volatile liquid.*

Still lower temperatures are produced by the evaporation of liquefied carbon dioxide, nitrogen monoxide, and other liquefied gases. When a jet of carbon dioxide is allowed to issue into the air from a narrow aperture, so intense a degree of cold is produced by the vaporisation of a part, that the remainder freezes to a solid, and falls in a shower of snow. By suffering this jet of liquid to flow into the metal box shown in fig. 32, a large quantity of the solid oxide may be obtained ; it closely resembles snow in appearance, and when held in the hand occasions a painful sensation of cold, while it gradually disappears. When it is mixed with a little ether, and poured upon a mass of mercury, the latter is almost instantly frozen, and in this way pounds of the solidified metal may be obtained. The addition of the ether facilitates the contact of the carbon dioxide with the mercury.

The temperature of a mixture of solid carbon dioxide and ether in the air, measured by a spirit-thermometer, was found to be − 106° F. ; when the same mixture was placed beneath the receiver of an air-pump, and exhaustion rapidly made, the temperature sank to − 166° F. This was the method of obtaining extreme cold em-

* See Chemical News, Oct. 27th, 1882, vol. xlii. p. 192.

ployed by Faraday in his last experiments on the liquefaction of gases, and recently extended, as already observed, to the liquefaction and solidification of other gases previously regarded as permanent.

Determination of the Specific Gravity of Gases and Vapours.

To determine the specific gravity of a gas, a large glass globe is filled with the gas to be examined, in a perfectly pure and dry state, having a known temperature, and an elastic force equal to that of the atmosphere at the time of the experiment. The globe so filled is weighed. It is then exhausted at the air-pump as far as possible, and again weighed. Lastly, it is filled with dry air, the temperature and pressure of which are known, and its weight once more determined. On the supposition that the temperature and elasticity are the same in both cases, the specific gravity is at once obtained by dividing the weight of the gas by that of the air.

The globe or flask must be made very thin, and fitted with a brass cap, surmounted by a small but well-fitting stop-cock. A delicate thermometer should be placed in the inside of the globe, secured to the cap. The gas must be generated at the moment, and conducted at once into the previously exhausted vessel, through a long tube filled with fragments of pumice moistened with oil of vitriol, or some other extremely hygroscopic substance, by which it is freed from all moisture. As the gas is necessarily generated under some pressure, the elasticity of that contained in the filled globe will slightly exceed the pressure of the atmosphere; and this is an advantage, since, by opening the stop-cock for a single instant, when the globe has attained an equilibrium of temperature, the tension becomes exactly that of the air, so that all barometrical correction is avoided, unless the pressure of the atmosphere should vary sensibly during the time occupied by the experiment. It is hardly necessary to observe that the greatest care must also be taken to purify and dry the air used as the standard of comparison, and to bring both gas and air as nearly as possible to the same temperature, so as to obviate the necessity of a correction, or at least to reduce almost to nothing the errors involved by such a process.

VAPOURS.—1. *Dumas' Method.* This method consists in determining the weight of a given volume of the vapour at a known pressure and temperature. A glass globe about three inches in diameter, having its neck softened and drawn out in the blowpipe flame, is accurately weighed. About 6 or 7 grams of the volatile liquid are then introduced, by gently warming the globe and dipping the point into the liquid, which is then forced upwards by the pressure of the air as the vessel cools. The globe is heated in a bath of water, oil, or melted paraffin to a temperature from 30° to 50° above the boiling point of the liquid, in order to bring the vapour as nearly as possible into the state in which it obeys the laws of gaseous expansion and contraction by alteration of pressure and temperature.

The liquid is then rapidly converted into vapour, which escapes by the narrow orifice, chasing before it the air of the globe. When the issue of vapour has wholly ceased, and the temperature of the bath appears nearly uniform, the open extremity of the point is sealed by a small blowpipe flame. The globe is removed from the bath, suffered to cool, cleansed if necessary, and weighed, after which the neck is broken off beneath the surface of water which has been boiled and cooled out of contact of air, or (better) under mercury. The liquid enters the globe, and, if the expulsion of the air by the vapour has been complete, fills it; if otherwise, an air-bubble is left, whose volume can be easily ascertained by pouring the liquid from the globe into a graduated jar, and then refilling the globe, and repeating the same observation, whereby also the capacity of the vessel is determined.

Fig. 35.

From these data the vapour-density (D) may be calculated by means of the formula:

$$D = \frac{P + Vn_t}{(V - v)\,n'_t}.$$

P = difference of weight (in grams) between the globe filled with air and when filled with vapour.

V = capacity of globe in cubic centimeters.

n_t = weight of one cubic centimeter of air at the temperature at which the globe filled with air was weighed.

n'_t = weight of one cubic centimeter of air at the temperature of sealing the globe.

The values of n_t and n'_t (in grams) for every five degrees centigrade from 0° to 300° are given in the Appendix, Table VII.*

In very exact experiments account must be taken of the change of capacity of the glass globe by the high temperature of the bath. When this correction is neglected, the density of the vapour will come out a little too high. The error of the mercurial thermometer at high temperatures is, however, in the opposite direction.

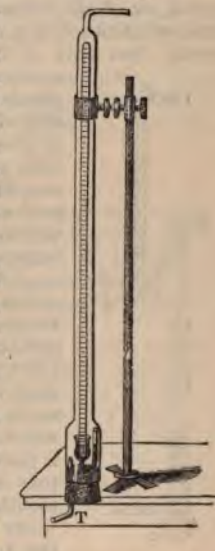
The preceding method is applicable to the determination of the vapour-densities of all substances whose boiling points are within the range of the mercurial thermometer, that is to say, not exceeding 300° C., and therefore to nearly all volatile organic compounds; indeed, there are but few such compounds which can bear higher temperatures without decomposition. But for mineral substances, such as sulphur, iodine, volatile metallic chlorides, &c., it is often

* The table here referred to is an abstract of one drawn up by C. Greville Williams for every degree of temperature between the above limits. (See Watts's Dictionary of Chemistry, vol. v. p. 370.)

sary to employ much higher temperatures; and for such cases dification of the process has been devised by Deville and t. It consists in using a globe of porcelain instead of glass, ng it in the vapour of a substance whose boiling point is known onstant, and sealing the globe by the flame of the oxy-hydrogen pipe. The vapours employed for this purpose are those of ury, which boils at 350°: of sulphur, which boils at 440°; of ium, boiling at 860°; and of zinc, boiling at 1040°. The use of liquids of constant boiling point obviates the necessity of deter- ng the temperature in each experiment, which at such degrees at would be very difficult.

Gay-Lussac's Method.—This method consists in ascertaining olume occupied by a given weight of a substance when con- d into vapour at a known temperature and pressure. It is readily performed with the apparatus contrived by Dr. A. W. ann (fig. 36). A graduated glass tube about a meter long and 20 mm. wide, is filled with mercury nverted in the little cup A, whereby a netric vacuum 20 to 30 mm. high is d at the top. The long tube is enclosed ther tube 30 to 40 mm. wide and 80 mm. long, drawn out at the top to a cting tube of moderate width, which at at right angles, and connected with s or copper vessel in which water, ani- or other liquid can be boiled. The part of the long tube is widened and upon a large cork, through which an escape tube T. By this arrange- a stream of vapour of water, aniline, er volatile liquid can be made to pass gh the space between the two tubes, to keep the upper part of the baro- -tube at the temperature required for etermination. The substance whose r-density is to be determined, is intro- into the barometric vacuum in small tubes fitted with ground stoppers, are forced out by the tension of the r. The great advantage of this me- s that, under the very small pressure ich the enclosed vapour is subjected ch may be reduced to 20 or even 10 eters of mercury—the determinations may be made at com- vely low temperatures. Thus, in the case of liquids boiling the ordinary pressure at 120° or even 150°, the vapour-density e accurately determined at the temperature of boiling water.

Fig. 36.



this mode of proceeding, we ascertain the volume which a weight W′ of substance occupies at a given temperature and

pressure; and dividing this by W, the weight of an equal volume V of air at the same pressure and temperature, which is given by the formula—

$$W = 0{\cdot}001293\,V \cdot \frac{1}{1 + 0{\cdot}00367\,T} \cdot \frac{P}{760},$$

0·001293 being the weight in grams of a cubic centimeter of air at 0° C. and 760 mm. pressure, and 0·00367 the coefficient of the thermal expansion of gases,* we obtain, for the density of the vapour, the expression—

$$D = \frac{W'}{W} = W' \frac{1 + 0{\cdot}00367\,T}{0{\cdot}001293} \cdot \frac{760}{P}.$$

3. *V. and C. Meyer's Method.*†—This is a very simple method of determining vapour-densities, founded on the same principle as the last, and applicable to substances either of low or of high boiling point. Its simplicity consists in this, that it does not require the determination either of the temperature to which the vapour is heated, or of the volume of the vapour at that temperature—both these quantities being eliminated in the expression for the vapour-density—but only of the volume of air displaced by the vapour evolved, this volume being measured at the atmospheric temperature. The apparatus (fig. 37) consists of a cylindrical glass bulb, *b*, having a capacity of about 100 c.c., to which is attached by fusion a tube 600 mm. long, terminating in a thimble-shaped enlargement, and having attached to it a side exit-tube *a*, by which the displaced air is transferred to a graduated tube standing in a small water-trough. For substances of boiling point not exceeding 310°, the bulb is heated in a glass tube, which terminates below in a bulb *c* containing various liquids, according to the volatility of the substance under experiment, viz., aniline (b. p. 181·5°), toluidine (202°), ethyl benzoate (212°), amyl benzoate (261°), diphenylamine (310°). The mode of working is as follows:—The bulb, into which a little ignited asbestos has been introduced, is fixed in position in the bath, the end of the exit-tube *a* dipping into the water-trough below the mouth of the graduated tube, which is filled with water and inverted. A cork is now inserted into the top of the vertical tube at *d*, and the extremity

Fig. 37.

* The values of the expression $\frac{1}{1 + 0{\cdot}00367\,T}$ have been calculated by C. Greville Williams for all temperatures from 1° to 150° C. (See Table VIII. in the Appendix.)

† Berichte der deutschen chemischen Gesellschaft, 1877, p. 2253.

of the exit-tube a is watched, to see that the temperature in the bulb is uniform. The cork is now taken out, the small tube containing the substance is dropped in, and the cork is quickly replaced. The first few bubbles of air are suffered to escape, but immediately afterwards the inverted tube is placed quickly over the point of the delivery-tube a. The substance is soon volatilised and displaces air, which issues in a rapid stream into the graduated tube; and as soon as air ceases to come over, the cork is removed, and the air collected is cooled and measured.

The density of the vapour is calculated by the formula

$$\frac{S \,.\, 760(1 + 0{\cdot}00365t)}{(B - w)V \,.\, 0{\cdot}001293} \text{ or } \frac{S(1 + 0{\cdot}00365t) \,.\, 587780}{(B - w)V},$$

in which S denotes the weight of substance, t the temperature of the water, B the barometric pressure reduced to 0°, w the tension of aqueous vapour, and V the volume of air displaced.

For temperatures above 310°, a bath of molten lead is employed; and for determining the vapour-densities of inorganic compounds which volatilise only at a red heat or at still higher temperatures, the glass vessel is replaced by one of porcelain or platinum heated in a gas-furnace.

For other recently proposed methods of determining vapour-densities, see Roscoe and Schorlemmer's Treatise on Chemistry, vol. iii. pp. 94—100; and Watts's Dictionary of Chemistry, vol. viii. p. 2096.

Sources of Heat.

The first and greatest source of heat, compared with which all others are totally insignificant, is the sun. The luminous rays are accompanied by heat-rays, which, striking against the surface of the earth, raise its temperature; this heat is communicated to the air by convection, as already described, air and gases in general not being sensibly heated by the passage of the rays.

A second source of heat is supposed to exist in the interior of the earth. It has been observed that, in sinking mine-shafts, boring for water, &c., the temperature rises, in descending, at the rate, it is said, of about 1° F. ($\frac{5}{9}$° C. for every 45 feet, or 117° F. (65° C.) per mile. On the supposition that the rise continues at the same rate, the earth, at the depth of less than two miles, would have the temperature of boiling water; at nine miles, it would be red-hot; and at thirty or forty miles depth, all known substances would be in a state of fusion.*

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* The Artesian well at Grenelle, near Paris, has a depth of 1774·5 English feet; it is bored through the chalk basin to the sand beneath. The temperature of the water, which is exceedingly abundant, is 82° F.; the mean temperature of Paris is 51° F.; the difference is 31° F., which gives a rate of about 1° for 58 feet.

According to this idea, the earth must be looked upon as an intensely heated fluid spheroid, covered with a crust of solid badly conducting matter, cooled by radiation into space, and bearing somewhat the same proportion in thickness to the ignited liquid within, that the shell of an egg bears to its fluid contents. Without venturing to offer any opinion on this theory, it may be sufficient to observe that it is not positively at variance with any known fact; that the figure of the earth is really such as would be assumed by a fluid mass; and, lastly, that it offers the best explanation we have of the phenomena of hot springs and volcanic eruptions, and agrees with the chemical nature of their products.

Among the other sources of heat are chemical combination and mechanical work.

The disengagement of heat in the act of combination is a phenomenon of the utmost generality. The quantity of heat given out in each particular case is fixed and definite; its intensity is dependent upon the time over which the action is extended. Many admirable researches on this subject have been published; but their results will be more advantageously considered at a later part of this work, in connection with the laws of chemical combination.

Heat produced by Mechanical Work.—Heat and motion are convertible one into the other. The powerful mechanical effects produced by the elasticity of the vapour evolved from heated liquids afford abundant illustration of the conversion of heat into motion; and the production of heat by friction, by the hammering of metals, and in the condensation of gases (p. 50), shows with equal clearness that motion may be converted into heat.

In some cases the rise of temperature thus produced appears to be due to a diminution of heat-capacity in the body operated upon, as in the case of a compressed gas just alluded to. Malleable metals, also, as iron and copper, which become heated by hammering or powerful pressure, are found thereby to have their density sensibly increased, and their capacity for heat diminished. A soft iron nail may be made red hot by a few dexterous blows on an anvil; but the experiment cannot be repeated until the metal has been *annealed*, and in that manner restored to its former physical state.

But the amount of heat which can be developed by mechanical force is, in most cases, out of all proportion to what can be accounted for in this way. Sir H. Davy melted two pieces of ice by rubbing them together in a vacuum at the temperature of 0°; and Count Rumford found that the heat developed by the boring of a brass cannon was sufficient to bring to the boiling point two and a half gallons of water, while the dust or shavings of metal cut by the borer weighed only a few ounces. In these and all similar cases the heat appears as a direct result of the force expended; the motion is converted into heat.

The connection between heat and mechanical force appears still more intimate when it is shown that they are related by an exact

numerical law, a given quantity of the one being always convertible into a definite amount of the other. The first approximate determination of this most important numerical relation was made by Count Rumford in the manner just alluded to. A brass cylinder enclosed in a box containing a known weight of water at 60° F. was bored by a steel borer made to revolve by horse power, and the time was noted which elapsed before the water was raised to the boiling point by the heat resulting from the friction. In this manner it was found that the heat required to raise the temperature of a pound of water by 1° F. is equivalent to 1034 times the force expended in raising a pound weight one foot high, or to 1034 "foot-pounds," as it is technically expressed. This estimate is now known to be too high, no account having been taken of the heat communicated to the containing vessel, or of that which was lost by dispersion during the experiment.

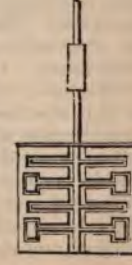
For the most exact determinations of the mechanical equivalent of heat, we are indebted to the careful and elaborate researches of Dr. J. P. Joule. From experiments made in the years 1840–43 on the relations between the heat and mechanical power generated by the electric current, Dr. Joule was led to conclude that the heat required to raise the temperature of a pound of water 1° F. is equivalent to 838 foot-pounds. This he afterwards reduced to 772; and a nearly equal result was afterwards obtained by experiments on the condensation and rarefaction of gases; but this estimate has since been found to be likewise too great.

The most trustworthy results are obtained by measuring the quantity of heat generated by the friction between solids and liquids. It was for a long time believed that no heat was evolved by the friction of liquids and gases; but in 1842 Meyer showed that the temperature of water may be raised 22° or 23° F. by agitating it. The warmth of the sea after a few days of stormy weather is also probably an effect of fluid friction.

The apparatus employed by Dr. Joule for the determination of this important constant, by means of the friction of water, consisted of a brass paddle-wheel furnished with eight sets of revolving vanes, working between four sets of stationary vanes. This revolving apparatus, of which fig. 38 shows a horizontal, and fig. 39 a vertical section, was firmly fitted into a copper vessel (see fig. 40) containing water, in the lid of which were two necks, one for the axis to revolve in without touching, the other for the insertion of a thermometer. A similar apparatus, but made of iron, and of smaller size, having six rotatory and eight

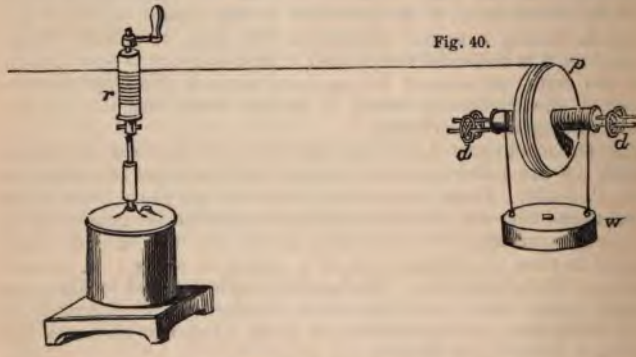
Fig. 38.

Fig. 39.



sets of stationary vanes, was used for the experiments on the friction of mercury. The apparatus for the friction of cast-iron consisted of a vertical axis carrying a bevelled cast-iron wheel, against which a bevelled wheel was pressed by a lever. The wheels were enclosed in a cast-iron vessel filled with mercury, the axis passing through the lid. In each apparatus motion was given to the axis by the descent of leaden weights W (fig. 40) suspended by strings from the axes of two wooden pulleys, one of which is shown at p, their

Fig. 40.



axes being supported on friction wheels d d, and the pulleys being connected by fine twine with a wooden roller r, which, by means of a pin, could be easily attached to or removed from the friction apparatus.

The mode of experimenting was as follows:—The temperature of the frictional apparatus having been ascertained, and the weights wound up, the roller was fixed to the axis, and the precise height of the weights ascertained; the roller was then set at liberty, and allowed to revolve till the weights touched the floor. The roller was then detached, the weights wound up again, and the friction renewed. This having been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the apartment was ascertained by observations made at the beginning, middle, and end of each experiment. Corrections were made for the effects of radiation and conduction; and, in the experiments with water, for the quantities of heat absorbed by the copper vessel and the paddle-wheel. In the experiments with mercury and cast-iron, the heat-capacity of the entire apparatus was ascertained by observing the heating effect which it produced on a known quantity of water in which it was immersed. In all the experiments, corrections were also made for the velocity with which the weights came to the ground, and for the friction and rigidity of the strings. The thermometers used were

capable of indicating a variation of temperature as small as $\frac{1}{200}$ of a degree Fahrenheit.

The following table contains a summary of the results obtained by this method. The second column gives the results as they were obtained in air; in the third column the same results corrected for a vacuum:—

Material employed.	Equivalent in air.	Equivalent in vacuum.	Mean.
Water . . .	773·640	772·692	772·692
Mercury . . .	773·762	772·814	774·083
	776·303	775·352	
Cast-iron . . .	776·997	776·045	774·987
	774·880	774·930	

In the experiments with cast-iron, the friction of the wheels produced a considerable vibration of the framework of the apparatus, and a loud sound; it was therefore necessary to make allowance for the quantity of force expended in producing these effects. The number 772·692, obtained by the friction of water, is regarded as the most trustworthy; but even this may be a little too high; because even in the friction of fluids it is impossible entirely to avoid vibration and sound. The conclusions deduced from these experiments are—

1. *That the quantity of heat produced by the friction of bodies, whether liquid or solid, is always proportional to the force expended.*

2. *That the quantity of heat capable of increasing the temperature of* 1 *lb. of water (weighed in vacuo, and between* 55° *and* 60°) *by* 1° *F., requires for its evolution the expenditure of a mechanical force represented by the fall of* 772 *lbs. through the space of* 1 *foot.*

Or, the heat capable of increasing the temperature of 1 *gram of water by* 1° *C., is equivalent to a force represented by the fall of* 423·66 *grams through the space of* 1 *meter. This is consequently the effect of "a unit of heat."*

Experiments made by other philosophers on the work done by a steam-engine, on the heat evolved by an electro-magnetic engine at rest and in motion, and on the heat evolved in the circuit of a voltaic battery and in a metallic wire through which an electric current is passing, have given values for the mechanical equivalent of heat very nearly equal to the above.

Dynamical Theory of Heat.

For a very long time two rival theories have been held regarding the nature of heat: on the one hand, heat has been viewed as having a material existence, though differing from ordinary matter in being without weight, and in other respects; on the other hand, it has been regarded as a state or condition of ordinary matter, and generally as a condition of motion. From the latter part of the last

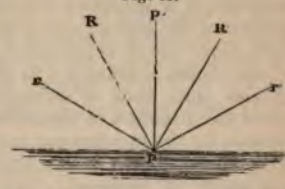
LIGHT.

Two views have been entertained respecting the nature of light. Newton imagined that luminous bodies emit, or shoot out, infinitely small particles in straight lines, which, by penetrating the transparent part of the eye and falling upon the nervous tissue, produce vision. Other philosophers drew a parallel between the properties of light and those of sound, and considered that, as sound is certainly the effect of undulations, or little waves, propagated through elastic bodies in all directions, so light might be nothing more than the consequence of similar undulations transmitted with inconceivable velocity through a highly elastic medium, of excessive tenuity, filling all space, and occupying the intervals between the particles of material substances. To this medium they gave the name of *ether*. The wave hypothesis of light is at present generally adopted. It is in harmony with all the known phenomena discovered since the time of Newton, not a few of which were first deduced from the undulatory theory, and afterwards verified by experiment. Several well-known facts are in direct opposition to the theory of emission.

A ray of light emitted from a luminous body proceeds in a straight line, and with extreme velocity. Certain astronomical observations afford the means of approximating to a knowledge of this velocity. The satellites of Jupiter revolve about the planet in the same manner as the moon about the earth, and the time of revolution of each satellite is exactly known from its periodical entry into or exit from the shadow of the planet. The time required by one is only 42 hours. Römer, the astronomer of Copenhagen, found that this period appeared to be longer when the earth, in its passage round the sun, moved from the planet Jupiter; and, on the contrary, he observed that the periodic time appeared to be shorter when the earth moved in the direction towards Jupiter. The difference, though very small for a single revolution of the satellite, increases, by the addition of many revolutions, during the passage of the earth from its nearest to its greatest distance from Jupiter, that is, in about half a year, till it amounts to 16 minutes and 16 seconds. Römer concluded from this, that the light of the sun, reflected from the satellite, required that time to pass through a distance equal to the diameter of the orbit of the earth; and since this space is little short of 200 millions of miles, the velocity of light cannot be less than 200,000 miles in a second of time. It will be seen hereafter that this rapidity of transmission is rivalled by that of electricity. Another astronomical phenomenon, observed and correctly explained by Bradley, the aberration of the fixed stars, leads to the same result. Physicists have, moreover, succeeded in measuring the velocity of light for terrestrial, and indeed comparatively small distances; the results of these experiments essentially correspond with those given by astronomical observations.

REFLECTION.—When a ray of light falls upon a boundary between two media, a part of it, and, in exceptional cases, the whole, is reflected into the first medium, whilst the other part penetrates into the second medium.

Fig. 41.



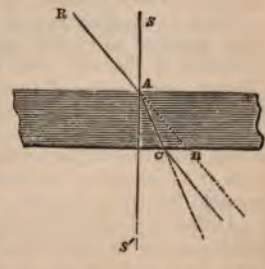
The law of regular reflection is extremely simple. If a line be drawn perpendicular to the surface upon which the ray falls, and the angle contained between the ray and the perpendicular be measured, it will be found that the ray, after reflection, takes such a course as to make with the perpendicular an equal angle on the opposite side of the latter. A ray of light, R, falling at the point P, will be reflected in the direction PR', making the angle R'PP' equal to the angle RPP'; and a ray from the point *r* falling upon the same spot will be reflected to *r'* in virtue of the same law. Further, it is to be observed, that the incident and reflected rays are always contained in the same normal plane.

The same rule holds good if the mirror be curved, as a portion of a sphere, the curve being considered as made up of a multitude of little planes. Parallel rays cease to be so when reflected from curved surfaces, becoming divergent or convergent according as the reflecting surface is convex or concave.

Bodies with rough and uneven surfaces, the smallest parts of which are inclined towards each other without order, reflect the light diffused. The perception of bodies depends upon the diffused reflected light.

REFRACTION.—It has just been stated that light passes in straight lines; but this is true only so long as the medium through which it travels preserves the same density and the same chemical nature: when this ceases to be the case, the ray of light is bent from its course into a new one, or is said to be *refracted*.

Fig. 42.



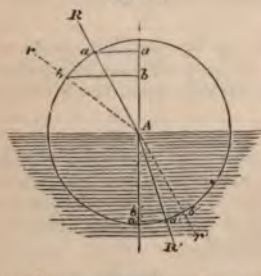
Let R (fig. 42) be a ray of light falling upon a plate of some transparent substance with parallel sides, such as a piece of thick plate glass,—in short, any transparent homogeneous material which is either non-crystalline, or crystallises in the regular system; and let A be its point of contact with the upper surface. The ray, instead of holding a straight course and passing into the glass in the direction A B, will be bent downwards to C; and, on leaving the glass, and issuing into the air on the other side, it will again be bent, but in the opposite direction, so as to make it parallel

to the continuation of its former track, provided there be one and the same medium on the upper and lower side of the plate. The general law is thus expressed :—When the ray passes from a rare to a denser medium, it is usually refracted *towards* a line perpendicular to the surface of the latter; and conversely, when it leaves a dense medium for a rarer one, it is refracted *from* a line perpendicular to the surface of the denser substance; in the former case the angle of incidence is greater than that of refraction; in the latter, it is less. In both cases the direction of the refracted ray is in the plane R A S, which is formed by the incident ray and the perpendicular S A drawn from the spot where the ray is refracted. The angle R A S = B A S′, is called the angle of incidence; the angle C A S′ the angle of refraction. The difference of these two angles, that is, the angle C A B, is the refraction.

The amount of refraction, for the same medium, varies with the obliquity with which the ray strikes the surface. When perpendicular to the latter, the ray passes without change of direction at all; and in other positions, the refraction increases with the obliquity.

Let R (fig. 43) represent a ray of light falling upon the surface of a mass of plate glass at the point A. From this point let a perpendicular fall and be continued into the new medium, and around the same point, as a centre, let a circle be drawn. According to the law just stated, the refraction must be towards the perpendicular; in the direction A R′ for example. Let the lines a—a, a'—a', at right angles to the perpendicular, be drawn, and their length compared by means of a scale of equal parts, and noted : their length will, in the case supposed, be in proportion of 3 to 2. These lines are termed the *sines* of the angles of incidence and refraction respectively.

Fig. 43.



Now let another ray be taken, such as r; it is refracted in the same manner to r', the bending being greater from the increased obliquity of the ray; but what is very remarkable, if the sines of the two new angles of incidence and refraction be again compared, they will still be found to bear to each other the proportion of 3 to 2. The fact is expressed by saying, that so long as the light passes from one to the other of the same two media, the *ratio of the sines of the angles of incidence and refraction is constant.* This ratio is called the *index of refraction.*

Different bodies possess different refractive powers; generally speaking, the densest substances refract most. Combustible bodies *have been noticed* to possess greater refractive power than their *density would indicate*, and from this observation Newton predicted

the combustible nature of the diamond long before anything was known respecting its chemical nature.

The method adopted for describing the comparative refractive power of different bodies, is to state the ratio borne by the sine of the angle of incidence in the first medium at the boundary of the second, to the sine of the angle of refraction in this second medium; this is called the *index of refraction* of the two substances; it is greater or less than unity, according as the second medium is denser or rarer than the first. In the case of air and plate glass the index of refraction is 1·5.

When the index of refraction of any particular substance is once known, the effect of the latter upon a ray of light entering it in any position can be calculated by the law of sines. The following table exhibits the indices of refraction of several substances, supposing the ray to pass into them from the air :—

Substances.	Index of refraction.	Substances.	Index of refraction.
Tabasheer*	1·10	Garnet	1·80
Ice	1·30	Glass with much oxide of lead	1·90
Water	1·34	Zircon	2·00
Fluor spar	1·40	Phosphorus	2·20
Plate glass	1·50	Diamond	2·50
Rock-crystal	1·60	Chromate of lead	3·00
Crysolite	1·69	Cinnabar	3·20
Bisulphide of carbon	1·70		

When a luminous ray enters a mass of substance differing in refractive power from the air, and whose surfaces are not parallel, it becomes permanently deflected from its course and altered in its direction. It is upon this principle that the properties of prisms and lenses depend. To take an example.—Fig. 44 represents a triangular prism of glass, upon the side of which the ray of light R may be supposed to fall. This ray will of course be refracted, on entering the glass, towards a line perpendicular to the first surface, and again, from a line perpendicular to the second surface on emerging into the air. The result is the deflection *a c* R, which is equal to the sum of the two deflections which the ray undergoes in passing through the prism.

Fig. 44.

A convex lens is thus enabled to converge rays of light falling upon it, and a concave lens to separate them more widely; each separate part of the surface of the lens producing its own independent effect.

DISPERSION.—The light of the sun and of celestial bodies in general, as well as that of the electric spark and of all ordinary flames, is

* *A siliceous deposit* in the joints of the bamboo.

of a compound nature. If a ray of light from any of the sources mentioned be admitted into a dark room by a small hole in a shutter, or otherwise, and suffered to fall upon a glass prism, in the manner shown in fig. 45, it will not only be refracted from its

Fig. 45.

straight course, but will be decomposed into a number of coloured rays, which may be received upon a white screen placed behind the prism. When solar light is employed, the colours are extremely brilliant, and spread into an oblong space of considerable length.

The prism being placed with its base upwards, as in fig. 45, the upper part of this image, or *spectrum*, will be violet and the lower red, the intermediate portion, commencing from the violet, being indigo, blue, green, yellow, and orange, all graduating imperceptibly into each other. This is the celebrated experiment of Sir Isaac Newton; from it he drew the inference that white light is composed of seven primitive colours, the rays of which are differently refrangible by the same medium, and hence capable of being thus separated. The violet rays are most refrangible, and the red rays least.*

Bodies of the same mean refractive power do not always equally disperse or spread out the differently coloured rays to the same extent; because the principal yellow or red rays, for instance, are equally refracted by two prisms of different materials, it does not follow that the blue or the violet will be similarly affected. Hence, prisms of different varieties of glass, or other transparent substances, give, under similar circumstances, very different spectra,

* The colours of natural objects are supposed to result from the power possessed by their surfaces of absorbing some of the coloured rays, while they reflect or transmit, as the case may be, the remainder of the rays. Thus an object appears red because it absorbs or causes to disappear the yellow and blue rays composing the white light by which it is illuminated. Any colour which remains after the deduction of another colour from white light, is said to be *complementary* to the latter. Complementary colours, when acting simultaneously, reproduce white light. Thus in the example already quoted, red and green are complementary colours. The *fact of* complementary colours giving rise to white light may be readily *illustrated by mixing* in appropriate quantities a rose-red solution of cobalt *and green solution* of nickel; the resulting liquid is nearly colourless.

both as respects the length of the image, and the relative extent of the coloured bands.

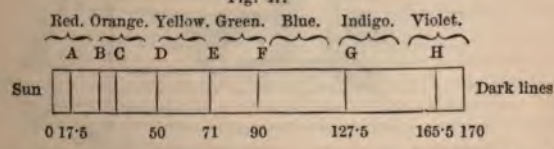
The appearance of the spectrum may also vary with the nature of the source of light: the investigation of these differences, however, involves the use of a more delicate apparatus. Fig. 46 shows the principle of such an apparatus, which is called a *spectroscope*.

Fig. 46.

The light, passing through a fine slit, *s*, impinges upon a flint-glass prism, *p*, by which it is dispersed. The decomposed light emerges from the prism in several directions between *r* (red rays) and *v* (violet rays); and the spectrum thus produced is observed by the telescope *t*, which receives only part of it at once; but the several parts may be readily examined by turning slightly either the prism or the telescope.

If the solar spectrum be examined in this manner, numerous dark lines parallel with the edge of the prism are observed. They were discovered in 1802 by Dr. Wollaston, and subsequently more minutely investigated by Fraunhofer. They are generally known as Fraunhofer's lines. These dark lines, which exist in great numbers, and of very varying strength, are irregularly distributed over the whole spectrum. Some of them, in consequence of their peculiar strength and their relative positions, may always be easily recognised. Fig. 47 shows the relative positions of the more conspicuous lines on a scale divided into 170 equal parts (*see* also the frontispiece to this volume). The same dark lines, though paler, and much more difficult to recognise, are observed in the spectrum of

Fig. 47.



planets lighted by the sun; for instance, in the light emanating from Venus. On the other hand, the dark lines observed in the spectra which are produced by the light emanating from fixed stars—from Sirius, for instance—differ in position from those previously mentioned.

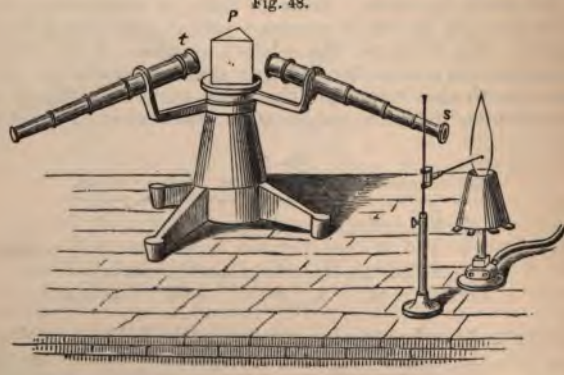
Sources of light which contain no volatile constituents—incan-

descent platinum wire, for example—furnish continuous spectra, exhibiting no such lines. But if volatile substances be present in the source of light, bright lines are observed in the spectrum, which are frequently characteristic of the volatile substances.

Professor Plücker, of Bonn, has investigated the spectra which are produced by the electric light when developed in very rarefied gases. He found the bright lines and the dark stripes between the lines to vary considerably with different gases. When the electric light was developed in a mixture of two gases, the spectrum thus obtained exhibited simultaneously the peculiar spectra belonging to the two gases of which the mixture consisted. When the experiment was made in gaseous compounds capable of being decomposed by the electric current, this decomposition was indicated by the spectra of the separated constituents becoming perceptible.

Many years ago the spectra of coloured flames were examined by Sir John Herschel, Fox Talbot, and W. A. Miller. More recently results of the greatest importance have been obtained by Kirchhoff and Bunsen, who have investigated the spectra furnished by the incandescence of volatile substances: these researches have enriched chemistry with a new method of analysis, the analysis by spectrum observations. In order to recognise one of the metals of the alkalis or of the alkaline earths, it is generally sufficient to introduce a minute quantity of a moderately volatile compound of the metal, on the loop of a platinum wire, into the edge of the very hot, but scarcely luminous flame, of a mixture of air and coal-gas, and to examine the spectrum which is furnished by the flame containing the vapour of the metal or its compound. Fig. 48 exhibits

Fig. 48.



the apparatus which is used in performing experiments of this description. The light of the flame in which the metallic compound is evaporated passes through the fine slit in the disc, *s*, into a tube,

the opposite end of which is provided with a convex lens. This lens collects the rays diverging from the slit, and throws them parallel upon the prism, *p*. The light is decomposed by the prism, and the spectrum thus obtained is observed by means of the telescope, which may be turned round the axis of the stand carrying the prism. Foreign light is excluded by an appropriate covering.

The limits of this elementary treatise do not permit us to describe the ingenious arrangements which have been contrived for sending the light from different sources through the same prism at different heights, whereby their spectra, the solar spectrum, for instance, and that of a flame, may be placed in a parallel position, the one above the other, and thus be compared.* The spectra of flames in which different substances are volatilised frequently exhibit such characteristically distinct phenomena, that they may be used with the greatest advantage for the discrimination of these substances. Thus the spectrum of a flame containing sodium (Na) exhibits a bright line on the yellow portion, the spectrum of potassium (K) a characteristic bright line at the extreme limit of the red, and another at the opposite violet limit of the spectrum. Lithium (Li) shows a bright brilliant line in the red, and a paler line in the yellow portion; strontium (Sr) a bright line in the blue, one in the orange, and six less distinct ones in the red portion of the spectrum. The frontispiece exhibits the most remarkable of the dark lines of the solar spectrum (Fraunhofer's lines), and the position of the bright lines in the spectra of flames containing the vapours of compounds of the metals of the alkalis and alkaline earths, also of the metals thallium and indium.

The delicacy of these spectral reactions is very considerable, but unequal in the case of different metals. The presence of $\frac{1}{200{,}000{,}000}$ grain of sodium in the flame is still easily recognisable by the bright yellow line in the spectrum. Lithium, when introduced in the form of a volatile compound, imparts to the flame a red colour; but this coloration is no longer perceptible when a volatile sodium compound is simultaneously present, the yellow coloration of the flame predominating under such circumstances. But when a mixture of one part of lithium and 1000 parts of sodium is volatilised in a flame, the spectrum of the flame exhibits, together with the bright yellow sodium line, likewise the red line characteristic of lithium. The observation of bright lines not belonging to any of the previously known bodies has led to the discovery of new elements. Thus, Bunsen and Kirchhoff, when examining the spectrum of the flame in which a mixture of alkaline salts was evaporated, observed some bright lines, which could not be attributed to any of the known elements, and were thus led to the discovery of the two new metals,

* See the article "Spectral Analysis," by Prof. Roscoe, in Watts's Dictionary of Chemistry, vol. v.

cæsium and rubidium. By the same method a new element, thallium, has been more recently discovered by Mr. Crookes; another, called indium, by Reich and Richter; a third, called gallium, by Lecoq de Boisbaudran; and several new earth-metals, by Cleve, Delafontaine, Marignac, and Nilson.

For the examination of the bright lines in the spectra of metals, the electric spark may be conveniently employed as a source of light. Small quantities of the metal are invariably volatilised; and the spectrum developed by the electric light exhibits the bright lines characteristic of the metal employed. These lines were observed by Wheatstone as early as 1835. This method of investigation is more especially applicable to the examination of the spectra of the heavy metals. The spark passes between two points of the metal or between two small cones of pure porous carbon impregnated with a solution of a compound of the metal.

By a series of theoretical considerations, Professor Kirchhoff has arrived at the conclusion that the spectrum of an incandescent gas is reversed—*i.e.*, that the bright lines become dark lines—if there be behind the incandescent gas a very luminous source of light, which by itself furnishes a continuous spectrum. Kirchhoff and Bunsen have fully confirmed this conclusion by experiment. Thus a volatile lithium salt produces, as just pointed out, a very distinct bright line in the red portion of the spectrum; but if bright sunlight, or the light emitted by a solid body heated to the most powerful incandescence, be allowed to fall through the flame upon the prism, the spectrum exhibits, in the place of this bright line, a black line similar in every respect to Fraunhofer's lines in the solar spectrum. In like manner the bright strontium line is reversed into a dark line. Kirchhoff and Bunsen have expressed the opinion that all the Fraunhofer lines in the solar spectrum are bright lines thus reversed. In their conception, the sun is surrounded by a luminous atmosphere, containing a certain number of volatilised substances, which would give rise in the spectrum to certain bright lines, if the light of the solar atmosphere alone could reach the prism; but the intense light of the powerfully incandescent body of the sun which passes through the solar atmosphere, causes these bright lines to be reversed and to appear as dark lines on the ordinary solar spectrum. Kirchhoff and Bunsen have thus been enabled to attempt the investigation of the chemical constituents of the solar atmosphere, by ascertaining the elements which, when in the state of incandescent vapour, develop bright spectral lines, coinciding with Fraunhofer's lines in the solar spectrum. Fraunhofer's line D (fig. 47) coincides most accurately with the bright spectral line of sodium, and may be artificially produced by reversing the latter; sodium would thus appear to a constituent of the solar atmosphere. Kirchhoff has proved, moreover, that sixty bright lines perceptible in the spectrum of iron correspond, both as to position and distinction, most exactly with the same number of dark lines in the solar spectrum, and, accordingly, he believes iron, in the state of vapour, to be present in

the solar atmosphere. In a similar manner this physicist has endeavoured to establish the presence of several other elements in the solar atmosphere.

Absorption Spectra.—The relative quantities of the several coloured rays absorbed by a coloured medium of given thickness may be observed by viewing a line of light through a prism and the coloured medium; the spectrum will then be seen to be diminished in brightness in some parts, and perhaps cut off altogether in others. This mode of observation is often of great use in chemical analysis, as many coloured substances when thus examined afford very characteristic spectra, the peculiarities of which may often be distinguished, even though the solution of the substance under examination contains a sufficient amount of coloured impurities to change its colour very considerably. The following method of making the observation is given by Professor Stokes.*

A small prism is to be chosen of dense flint glass, ground to an angle of 60°, and just large enough to cover the eye comfortably. The top and bottom should be flat, for convenience of holding the prism between the thumb and fore-finger, and laying it down on a table, so as not to scratch or soil the faces. A fine line of light is obtained by making a vertical slit in a board six inches square, or a little longer in a horizontal direction, and adapting to the aperture two pieces of thin metal. One of the metal pieces is movable, to allow of altering the breadth of the slit. About the fiftieth of an inch is a suitable breadth for ordinary purposes. The board and metal pieces should be well blackened.

On holding the board at arm's length against the sky or a luminous flame, the slit being, we will suppose, in a vertical direction, and viewing the line of light thus formed through the prism held close to the eye, with its edge vertical, a pure spectrum is obtained at a proper azimuth of the prism. Turning the prism round its axis alters the focus, and the proper focus is got by trial. The whole of the spectrum is not, indeed, in perfect focus at once, so that in scrutinising one part after another, it is requisite to turn the prism a little. When daylight is used, the spectrum is known to be pure by its showing the principal fixed lines; in other cases the focus is got by the condition of seeing distinctly the other objects, whatever they may be, which are presented in the spectrum. To observe the absorption spectrum of a liquid, an elastic band is put round the board near the top, and a test-tube containing the liquid is slipped under the band, which holds it in its place behind the slit. The spectrum is then observed just as before, the test-tube being turned from the eye.

To observe the whole progress of the absorption, different degrees of strength must be used in succession, beginning with a

* Chem. Soc. Jour. xvii. 306.

strength which does not render any part of the spectrum absolutely black, unless it be one or more very narrow bands, as otherwise the most distinctive features of the absorption might be missed. If the solution be contained in a wedge-shaped vessel instead of a test-tube, the progress of the absorption may be watched in a continuous manner by sliding the vessel before the eye. Some observers prefer using a wedge-shaped vessel in combination with the slit, the slit being perpendicular to the edge of the wedge. In this case each element of the slit forms an elementary spectrum corresponding with a thickness of the solution which increases in a continuous manner from the edge of the wedge, where it vanishes. This is the mode of observation adopted by Gladstone.*

Fig. 49 represents the effect produced in this way by a solution of chromic chloride, and fig. 50 that produced by a solution of potassium permanganate.

Fig. 49.

Fig. 50.

The right hand side of these figures corresponds with the red end of the spectrum ; the letters refer to Fraunhofer's lines. The lower part of each figure shows the pure spectrum seen through the thinnest part of the wedge ; and the progress of the absorption, as the thickness of the liquid increases, is seen by the gradual obliteration of the spectrum towards the upper part of the figures.

Fluorescence.—An examination into a peculiar mode of analysis of light, discovered by Sir John Herschel, in a solution of quinine sulphate, has within the last few years led to the discovery of a most remarkable fact. Professor Stokes has observed that light of certain refrangibility and colour is capable of experiencing a peculiar influence in being dispersed by certain media, and of undergoing

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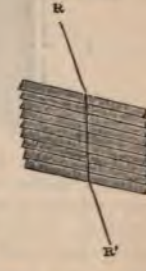
* Chem. Soc. Journ. x. 79.

thereby an alteration of its refrangibility and colour. This curious change, called fluorescence, can be produced by a great number of bodies, both liquid and solid, transparent and opaque. Frequently the change affects only the extreme limits; at other times larger portions; and in a few cases even the whole, or, at all events, the major part of the spectrum. A dilute solution of quinine sulphate, for instance, changes the violet and the dark-blue light to sky-blue; by a decoction of madder in a solution of alum all rays of higher refrangibility than yellow are converted into yellow; by an alcoholic solution of the colouring matter of leaves, all the rays of the spectrum become red. In all cases in which this peculiar phenomenon presented itself in a greater or less degree, Stokes observed that it consisted in a diminution of the refrangibility. Thus, rays of so high a degree of refrangibility, that they extend far beyond the extreme limits of the spectrum visible under ordinary circumstances, may be rendered luminous, and converted into blue and even red light.

Double Refraction and Polarisation.—A ray of common light made to pass through certain crystals of a particular order is found to undergo a very remarkable change. It becomes split or divided into two rays, one of which follows the general law of refraction, while the other takes a new and extraordinary course, dependent on the position of the crystal. This effect, which is called **double refraction**, is beautifully illustrated in the case of Iceland spar, or crystallised calcium carbonate. On placing a rhomb of this substance on a piece of white paper on which a mark or line has been made, the object will be seen double.

Again, if a ray of light be suffered to fall on a plate of glass at an angle of 56° 45′, the portion of the ray which suffers reflection will be found to have acquired properties which it did not before possess; for on throwing it, at the same angle, upon a second glass plate, it will be observed that there are two particular positions of the latter, namely, those in which the planes of incidence are at right angles to one another, when the ray of light is no longer reflected, but entirely refracted. Light which has suffered this change is said to be *polarised*.

Fig. 51.



The light which passes through the first or polarising plate is also, to a certain extent, in this peculiar condition, and by employing a series of similar plates held parallel to the first, this effect may be greatly increased; a bundle of fifteen or twenty such plates may be used with great convenience for the experiment. It is to be remarked, also, that the light polarised by transmission in this manner is in an opposite state to that polarised

ing the colour of the double plate uniform, when it has ceased to be so by the action of the sugar.

Faraday made the remarkable discovery that, if a very strong electric current be passed round a substance which possesses the property of circular polarisation, the amount of rotation is altered to a considerable degree.

Heating and Chemical Rays of the Solar Spectrum.—The luminous rays of the sun are accompanied, as already mentioned, by others which possess heating powers. If the temperature of the different-coloured spaces in the spectrum be tried with a delicate thermometer, it will be found to increase from the violet to the red extremity, and when the prism is of some particular kinds of glass, the greatest effect will be manifested a little beyond the visible red rays. The position of the greatest heating effect in the spectrum materially depends on the absorptive nature of the glass. Transparent though this medium is to the rays of light, it nevertheless absorbs a considerable quantity of the heat rays. Transparent rock-salt is almost without absorptive action on the thermal rays. In the spectrum obtained by passing the solar rays through prisms of rock-salt, the greatest thermal effect is found at a position far beyond the last visible red rays. It is inferred from this that the greater number of the heating rays are among the least refrangible components of the solar beam.

Again, it has long been known that chemical changes both of combination and of decomposition, but more particularly the latter, can be effected by the action of light. Chlorine and hydrogen combine at common temperatures only under the influence of light; and parallel cases occur in great numbers in organic chemistry. The blackening and decomposition of silver salts are familiar instances of the chemical powers of the same agent. Now, it is not always the luminous part of the ray which effects these changes; they are chiefly produced by certain invisible rays, which accompany the others, and are found most abundantly beyond the violet part of the spectrum. It is there that certain chemical effects are most marked, although the intensity of the light is exceedingly feeble. These chemically acting rays are sometimes called *actinic rays* (ακτις, a ray), and the chemical action of sunlight is called *actinism*; but these terms are not very well chosen. The chemical rays are thus directly opposed to the heating rays in the common spectrum in their degree of refrangibility, since they exceed all the others in this respect. The luminous rays, too, under peculiar conditions, exert decomposing powers upon silver salts. The result of the action of any ray depends, moreover, greatly on the physical state of the surface upon which it falls, and on the chemical constitution of the body; indeed, for every kind of ray a substance may be found which under particular circumstances will be affected by it; and thus it appears that the chemical functions are by no means confined to any set of rays to the exclusion of the rest.

Upon the chemical changes produced by light is based the art of *photography*. In the year 1802 Mr. Thomas Wedgwood proposed a method of copying paintings on glass, by placing behind them white paper or leather moistened with a solution of silver nitrate, which became decomposed and blackened by the transmitted light in proportion to the intensity of the latter; and Davy, in repeating these experiments, found that he could thus obtain tolerably accurate representations of objects of a texture partly opaque and partly transparent, such as leaves and the wings of insects, and even copy with a certain degree of success the images of small objects obtained by the solar microscope. These pictures, however, required to be kept in the dark, and could be examined only by candle-light, otherwise they became obliterated by the blackening of the whole surface, from which the silver salt could not be removed. These attempts at light-painting attracted but little notice till the year 1839, when Mr. Fox Talbot published his plan of "photogenic drawing." This consisted in exposing in the camera a paper soaked in a weak solution of common salt, and afterwards washed over with a strong solution of silver nitrate; the image thus obtained was a *negative* one, the lights being dark and the shadows light, and the pictures were fixed by immersion in a solution of common salt.

Many improvements have been made in this process. In 1841 Fox Talbot patented the beautiful process known as the "Talbotype or Calotype process," in which the paper is coated with silver iodide by dipping it first in silver nitrate, then in potassium iodide. Paper thus prepared is not sensitive *per se* to the action of light, but may be rendered so by washing it over with a mixture of silver nitrate and gallic or acetic acid. If it be exposed to the camera for two or three minutes, it does not receive a visible image (unless the light has been very strong); but still the compound has undergone a certain change by the influence of the light: for on subsequently washing it over with the mixture of silver nitrate and acetic or gallic acid, and gently warming it, a negative image comes out on it with great distinctness. This image is *fixed* by washing the paper with sodium thiosulphate (commonly called hyposulphite), which removes the whole of the silver iodide not acted upon by the light, and thus protects the picture from further change by exposure to light. The negative picture thus obtained is rendered transparent by placing it between two sheets of blotting-paper saturated with white wax, and passing a moderately heated smoothing-iron over the whole. It may then be used for printing *positive pictures* by laying it on a sheet of paper prepared with chloride or iodide of silver, and exposing it to the sun.

A most important step in the progress of photography was the substitution of a transparent film of iodised collodion or albumin spread upon glass, for the iodised paper used in Talbot's process, to receive the negative image in the camera. The process is thus rendered so much more certain and rapid, and the positive pictures

obtained by transferring the negative to paper prepared with chloride or iodide of silver, are found to be so much sharper in outline than when the transference occurs through paper, as in the talbotype process, that this method is now universally employed. In this process, as in that of the Calotype, the image produced in the camera is a latent one, and requires development with substances such as pyrogallic acid, or ferrous sulphate, which, having a tendency to absorb oxygen, induce, in presence of silver nitrate, the reduction of the chloride or iodide to the metallic state. For a description of the best apparatus and latest processes used in the collodion method, the reader may consult Hardwich's "Manual of Photographic Chemistry," and Captain Abney's "Instruction in Photography."

Sir John Herschel showed that a great number of other substances can be employed in these photographic processes by taking advantage of the deoxidising effects of certain portions of the solar rays. Paper washed with a solution of ferric salt becomes capable of receiving impressions of this kind, which may afterwards be made evident by potassium ferricyanide, or gold chloride. Vegetable colours are also acted upon in a very curious and apparently definite manner by the different parts of the spectrum.

The *daguerreotype*, the announcement of which was first made in the summer of 1839, by M. Daguerre, who had been occupied with this subject from 1826, if not earlier, is another remarkable instance of the decomposing effects of the solar rays. A clean and highly polished plate of silvered copper is exposed for a certain time to the vapour of iodine, and then transferred to the camera obscura. In the most improved state of the process, a very short time suffices for effecting the necessary change in the film of silver iodide. The picture, however, becomes visible only by exposing it to the vapour of mercury, which attaches itself, in the form of exceedingly minute globules, to those parts which have been most acted upon, that is to say, to the lights, the shadows being formed by the dark polish of the metallic plate. Lastly, the plate is washed with sodium thiosulphate, to remove the undecomposed silver iodide and render it permanent.

Since Daguerre's time this process has undergone considerable improvements; amongst these, we may mention the exposure of the plate to the vapour of bromine, by which the sensitiveness of the film is greatly increased, and the reduction of metallic gold upon the surface of the film during the process of fixing, by which the lights and shades of the picture are rendered more effective; but it is now completely superseded by photography.

Etching and lithographic processes, by combined chemical and photographic agency, promise to be of considerable utility. The earliest is that of Niepce: he applied a bituminous coating to a metal plate, upon which an engraving was superimposed. The light, being thus partially interrupted, acted unequally upon the varnish; a liquid hydro-carbon, *petroleum*, used as a solvent, removed the

bitumen wherever the light had not acted; the unprotected metal was bitten by an acid; and the plate could then be printed from in the usual way. Very successful results have also been obtained by M. Fizeau, who submits the daguerreotype to the action of a mixture of dilute nitric acid, common salt, and potassium nitrate, when the silver only is attacked, the mercurialised portion of the image resisting the acid; an etching is thus obtained following minutely the lights and shadows of the picture. To deepen this etching, the silver chloride formed is removed by ammonia, the plate is boiled in caustic potash and again treated with acid, and so on till the etching is of sufficient depth. Sometimes electro-gilding is resorted to, and an engraving acid is used to get still more powerful impressions.

Among recent results are those obtained by Mr. Talbot on steel plates: he uses a mixture of potassium bichromate and gelatin, which hardens by exposure to the light; the parts not affected are removed by washing. Platinum tetrachloride is used as an etching liquid: it has the advantage of biting with greater regularity than nitric acid.

The bitumen process of M. Niépce has been applied to lithographic stone; and positives obtained from negative talbotypes have been printed off by a modification of the ordinary lithographic process. M. Niépce finds that ether dissolves the altered bitumen, while petroleum or benzene attacks by preference the bitumen in its normal condition.

MAGNETISM.

A PARTICULAR species of iron ore has long been remarkable for its property of attracting small pieces of iron, and causing them to adhere to its surface; it is called loadstone, or magnetic iron ore.

If a piece of this loadstone be carefully examined, it will be found that the attractive force for particles of iron is greatest at certain particular points of its surface, while elsewhere it is much diminished, or even altogether absent. These attractive points are denominated poles, and the loadstone itself is said to be endowed with magnetic polarity.

If one of the pole-surfaces of a natural loadstone be rubbed in a particular manner over a bar of steel, its characteristic properties will be communicated to the bar, which will then be found to attract iron-filings like the loadstone itself. Further, the attractive force will appear to be greatest at two points situated very near the extremities of the bar, and least of all towards the middle. The bar of steel so treated is said to be magnetised, or to constitute an artificial magnet.

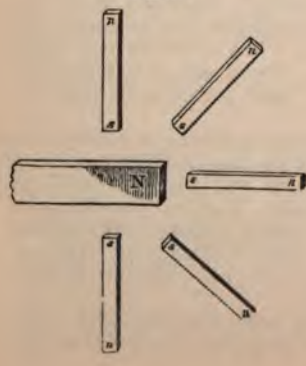
When a magnetised bar or natural magnet is suspended at its centre in any convenient manner, so as to be free to move in a hori-

zontal plane, it is always found to assume a particular direction with regard to the earth, one end pointing nearly north, and the other nearly south. This direction varies with the geographical position of the place, and is different also at the same place at different times. At London, in 1881, the needle pointed 18° 33′ west of the astronomical north. If the bar be moved from this position, it will tend to reassume it, and, after a few oscillations, will settle at rest as before. The pole which points towards the astronomical north is usually distinguished as the north pole of the bar, and that which points southward as the south pole.

A magnet, either natural or artificial, of symmetrical form, suspended in the presence of a second magnet, serves to exhibit certain phenomena of attraction and repulsion which deserve particular attention. When a north pole is presented to a south pole, or a south pole to a north, attraction ensues between them; the ends of the bars approach each other, and, if permitted, adhere with considerable force; when, on the other hand, a north pole is brought near a second north pole, or a south pole near another south pole, mutual repulsion is observed, and the ends of the bars recede from each other as far as possible. *Poles of an opposite name attract, and poles of a similar name repel each other.* Thus, a small bar or needle of steel, properly magnetised and suspended, and having its poles marked, becomes an instrument fitted not only to discover the existence of magnetic power in other bodies, but to estimate the kind of polarity affected by their different parts.

A piece of soft iron brought into the neighbourhood of a magnet acquires itself magnetic properties: the intensity of the power thus conferred depends upon that of the magnet, and upon the space which divides the two, becoming greater as that space decreases, and greatest of all in actual contact. The iron, under these circumstances, is said to be magnetised by *induction* or influence, and the effect, which reaches its maximum in an instant, is at once destroyed by removing the magnet.

Fig. 55.



When steel is substituted for iron in this experiment, the inductive action is hardly perceptible at first, and becomes manifest only after the lapse of a certain time: in this condition, when the steel bar is removed from the magnet, it retains a portion of the induced polarity. It becomes, indeed, a permanent magnet, similar to the first, and retains its peculiar properties for an indefinite time. This resistance which steel always offers in a

greater or less degree both to the development of magnetism and to its subsequent destruction, is called *specific coercive power.*

The rule which regulates the induction of magnetic polarity in all cases is exceedingly simple, and most important to be remembered. The pole produced is always of the opposite name to that which produced it, a north pole developing south polarity, and a south pole north polarity. The north pole of the magnet figured in the sketch induces south polarity in all the nearer extremities of the pieces of iron or steel which surround it, and a state similar to its own in all the more remote extremities. The iron thus magnetised is capable of exerting a similar inductive action on a second piece, and that upon a third, and so to a great number, the intensity of the force diminishing as the distance from the permanent magnet increases. It is in this way that a magnet is enabled to hold up a number of small pieces of iron, or a bunch of filings, each separate piece becoming for the time a magnet by induction.

Magnetic polarity, similar in degree to that which iron presents, has been found only in some of the compounds of iron, in nickel, and in cobalt.

Magnetic attractions and repulsions are not in the slightest degree interfered with by the interposition of substances destitute of magnetic properties. Thick plates of glass, shellac, metals, wood, or of any substances except those above mentioned, may be placed between a magnet and a suspended needle, or a piece of iron under its influence, the distance being preserved, without the least perceptible alteration in its attractive power, or force of induction.

One kind of polarity cannot be exhibited without the other. In other words, a magnetic pole cannot be isolated. If a magnetised bar of steel be broken at its neutral point, or in the middle, each of the broken ends acquires an opposite pole, so that both portions of the bar become perfect magnets; and, if the division be carried still further, if the bar be broken into a hundred pieces, each fragment will be a complete magnet, having its own north and south poles.

This experiment serves to show very clearly that the apparent polarity of the bar is the consequence of the polarity of each individual particle, the poles of the bar being merely points through which the resultants of all these forces pass; the largest magnet is made up of an immense number of little magnets regularly arranged side by side, all having their north poles looking one way, and their

Fig. 56.

south poles the other. The middle portion of such a system cannot possibly exhibit attractive or repulsive effects on an external body, because each pole is in close juxtaposition with one of an opposite

name and of equal power. Hence their forces will be exerted in opposite directions, and neutralise each other's influence. Such will not be the case at the extremities of the bar; there uncompensated polarity will be found, capable of exerting its specific power.

This idea of regular polarisation of particles of matter in virtue of a pair of opposite and equal forces, is not confined to magnetic phenomena; it is the leading principle in electrical science, and is constantly reproduced in some form or other in every discussion involving the consideration of molecular forces.

Artificial steel magnets are made in a great variety of forms; such as small light needles, mounted with an agate for suspension upon a fine point; straight bars of various kinds; bars curved into the shape of a horse-shoe, &c. All these have regular polarity communicated to them by certain processes of rubbing or touching with another magnet, which require care, but are not otherwise difficult of execution. When great power is wished for, a number of bars may be screwed together, with their similar ends in contact, and in this way it is easy to construct permanent steel magnets capable of sustaining great weights. To prevent the gradual destruction of magnetic force, which would otherwise occur, it is usual to arm each pole with a piece of soft iron or keeper, which, becoming magnetised by induction, serves to sustain the polarity of the bar, and in some cases even increases its energy.

Magnetism is not peculiar to these substances which have more especially been called magnetic, such as iron, nickel, cobalt, but it is the property of all metals, though to a much smaller degree. Very powerful magnets are required to show this remarkable fact. Large horse-shoe magnets, made by the action of the electric current, are best adapted for the purpose. The magnetic action on different substances which are capable of being easily moved, differs not only according to the size, but also according to the nature of the substance. In consequence of this, Faraday divides all bodies into two classes. He calls the one magnetic, or, better, *paramagnetic*, and the other *diamagnetic*.

The matter of which a paramagnetic (magnetic) body consists is attracted by both poles of the horse-shoe magnet; on the contrary, the matter of a diamagnetic body is repelled. When a small iron bar is hung by untwisted silk between the poles of the magnet, so that its long diameter can easily move in a horizontal plane, it arranges itself axially, that is, parallel to the straight line which joins the poles, or to the magnetic axis of the poles, assuming at the end which is nearest the north pole, a south pole, and at the end nearest the south pole, a north pole. Whenever the little bar is removed from this position, it returns, after a few oscillations, to its previous position. The whole class of paramagnetic bodies behave in a precisely similar way under similar circumstances, but in the intensity of the effects great differences occur.

Diamagnetic bodies, on the contrary, have their long diameters placed equatorially, that is, at right angles to the magnetic axis

They behave as if at the end opposite to each pole of the magnet the same kind of polarity existed.

In the first class of substances, besides iron, which is the best representative of the class, we have nickel, cobalt, manganese, chromium, cerium, titanium, palladium, platinum, osmium, aluminium, oxygen, and also most of the compounds of these bodies, most of them even when in solution. According to Faraday, the following substances are also feebly paramagnetic (magnetic),—paper, sealing-wax, Indian ink, porcelain, asbestos, fluorspar, minium, cinnabar, binoxide of lead, sulphate of zinc, tourmaline, graphite, and charcoal.

In the second class are placed bismuth, antimony, zinc, tin, cadmium, sodium, mercury, lead, silver, copper, gold, arsenic, uranium, rhodium, iridium, tungsten, phosphorus, iodine, sulphur, chlorine, hydrogen, and many of their compounds. Also, glass free from iron, water, alcohol, ether, nitric acid, hydrochloric acid, resin, wax, olive oil, oil of turpentine, caoutchouc, sugar, starch, gum, and wood. These are diamagnetic.

When diamagnetic and paramagnetic bodies are combined, their peculiar properties are more or less neutralised. In most of these compounds, occasionally in consequence of the presence of a very small quantity of iron, the peculiar magnetic power remains more or less in excess. Thus green bottle-glass, and many varieties of crown glass, are magnetic in consequence of the iron they contain.

In order to examine the magnetic properties of liquids, they are placed in very thin glass tubes, the ends of which are then closed by melting; they are then hung horizontally between the poles of the magnet. Under the influence of poles sufficiently powerful, they begin to swing, and according as the fluid contents are paramagnetic (magnetic) or diamagnetic, they assume an axial or equatorial position.

Faraday tried the magnetic condition of gases in different ways. One method consisted in making soap-bubbles with the gas which he wished to investigate, and bringing these near the poles. Soap and water alone is feebly diamagnetic. A bubble filled with oxygen was strongly attracted by the magnet. All other gases in the air are diamagnetic, that is, they are repelled. But, as Faraday has shown, in a different way, this partly arises from the paramagnetic (magnetic) property of the air. Thus he found that nitrogen, when this differential action was eliminated, was perfectly indifferent, whether it was condensed or rarefied, whether cooled or heated. When the temperature is raised, the diamagnetic property of gases in the air is increased. Hence the flame of a candle or of hydrogen is strongly repelled by the magnet. Even warm air is diamagnetic in cold air.

For some time it had been believed that crystallised bodies exhibited a special and peculiar behaviour when placed between the poles of a magnet. It appeared as though the magnetic directing power of the crystal had some peculiar relation to the position of its

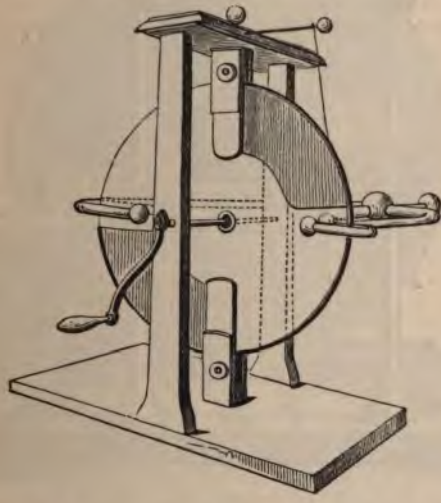
optic axis; so that, independently of the magnetic property of the substance of the crystal, if the crystal were positively optical, it possessed the power of placing its optic axis parallel with the line which joined the poles of the magnet, while optically negative crystals tried to arrange their axes at right angles to this line. This supposition is disproved by the excellent investigation of Tyndall and Knoblauch, who showed that exceptions to the above law are furnished by all classes of crystals, and proved that the action, instead of being independent of the magnetic nature of the mass, was completely reversed where, in isomorphous crystals, a magnetic constituent was substituted for a diamagnetic one. Rejecting the various new forces assumed, Tyndall and Knoblauch referred the observed phenomena to the modification of the magnetic force by structure, and they imitated the effects exactly by means of substances whose structure had been modified by compression. In a later investigation Tyndall demonstrated the fundamental principle on which those phenomena depend, showing that the *entire mass* of a magnetic body is most strongly attracted when the attracting force acts parallel to the line of compression; and that a diamagnetic substance is most strongly repelled when the repulsion acts along the same line. Hence when such a body is freely suspended in the magnetic field, the line of compression must set axially or equatorially, according as the mass is magnetic or diamagnetic. Faraday was the first to establish a differential action of this kind in the case of bismuth; Tyndall extended it to several magnetic and diamagnetic crystals, and showed that it was not confined to them, but was a general property of matter. It was also proved that for a fixed distance the attraction of a magnetic sphere, and the repulsion of a diamagnetic sphere, followed precisely the same law, both being exactly proportioned to the square of the exciting current.

The phenomena of diamagnetism naturally suggest the inquiry, whether the repulsion exerted by a magnetic pole on diamagnetic bodies is a force distinct from that of magnetism as exerted upon iron and other bodies of the magnetic class; or whether, on the other hand, the magnetic and diamagnetic conditions of matter are merely relative, so that all bodies are magnetic in different degrees, and the apparent repulsion of a diamagnetic body, such as bismuth, is merely the result of its being attracted by the magnet less than the particles of the surrounding medium, just as a balloon recedes from the earth because its weight is less than that of an equal bulk of the surrounding air. It is easy to show that the same body may appear magnetic or diamagnetic, according to the medium in which it is placed. Ferrous sulphate is a magnetic substance, and water is diamagnetic: hence it is possible, by varying the strength of an aqueous solution of this salt, to make it either magnetic, indifferent, or diamagnetic, when suspended in air. Again, a tube containing a solution of ferrous sulphate suspended horizontally within a jar also filled with a solution of the same salt, and placed between the poles of two powerful electro-magnets, will place itself axially or

insulated bodies. The maximum effect is produced when the rubber is connected by a chain or wire with the earth. If negative electricity be wanted, the rubber must be insulated and the conductor discharged.

Another form of the electrical machine consists of a circular plate of glass (fig. 62) moving upon an axis, and provided with two pairs

Fig. 62.



of cushions or rubbers, attached to the upper and lower parts of the wooden frame, and covered with amalgam, the plate moving between them with considerable friction. An insulated conductor, armed as before with points, discharges the plate as it turns, the rubber being at the same time connected with the ground by the woodwork of the machine, or by a strip of metal. This form of machine is preferred in all cases where considerable power is required; but for demonstrating the principles of the science, as in lecture-experiments, the cylinder machine is by far the more convenient form, as it affords the means of obtaining a positive or negative charge at pleasure.

A machine of much greater power than either of the preceding is that of Holtz, in which the development of the charge takes place much in the same manner as in the electrophorus. This machine, which may indeed be regarded as a revolving electrophorus, consists of two glass plates (fig. 63), one AA, fixed by means of four wooden rollers resting on glass axes and glass feet, while the other, BB, two inches less in diameter, turns on a horizontal glass axis passing

ELECTRICITY.

When glass, amber, or sealing-wax is rubbed with a dry cloth, it acquires the power of attracting light bodies, as feathers, dust, or bits of paper; this is the result of a new and peculiar condition of the body rubbed, called electrical excitation.

If a light downy feather be suspended by a thread of white silk, and a dry glass tube, excited by rubbing, be presented to it, the feather will be strongly attracted to the tube, adhere to its surface for a few seconds, and then fall off. If the tube be now excited anew, and presented to the feather, the latter will be strongly repelled.

The same experiment may be repeated with shellac or resin; the feather in its ordinary state will be drawn towards the excited body, and, after touching, again driven from it with a certain degree of force.

Now, let the feather be brought into contact with the excited glass, so as to be repelled by that substance, and let a piece of excited sealing-wax be presented to it: a degree of attraction will be observed far exceeding that exhibited when the feather is in its ordinary state. Or, again, let the feather be made repulsive for sealing-wax, and then the excited glass be presented: strong attraction will ensue.

The reader will at once see the perfect parallelism between the effects described and some of the phenomena of magnetism, the electrical excitement having a twofold nature, like the opposite polarities of the magnet. A body to which one kind of excitement has been communicated is attracted by another body in the opposite state, and repelled by one in the same state; the excited glass and resin being to each other as the north and south poles of a pair of magnetised bars.

To distinguish these two different forms of excitement, terms are employed which, although originating in some measure in theoretical views of the nature of the electrical disturbance, may be understood by the student as purely arbitrary and distinctive: it is customary to call the electricity manifested by glass rubbed with silk *positive* or *vitreous*, and that developed in the case of shellac, and bodies of the same class rubbed with flannel, *negative* or *resinous*. The kind of electricity depends in some measure upon the nature of the surface and the quality of the rubber; smooth and perfectly clean glass, rubbed with silk, becomes positive, but when ground or roughened by sand or emery, it acquires, under the same circumstances, a negative charge. Glass dried over a gas flame and rubbed with wool is generally also negative; and when dried over a fire of wood-charcoal it remains positive.

The repulsion shown by bodies in the same electrical state is taken advantage of to construct instruments for indicating electrical

excitement and pointing out its kind. Two balls of elder pith hung by threads or very fine metal wires, serve this purpose in many cases: they open out when excited, in virtue of their mutual repulsion, and show by the degrees of divergence the extent to which the excitement has been carried. A pair of gold leaves suspended from

Fig. 57.

Fig. 58.

a metal rod having a brass plate on its upper end constitute a much more delicate arrangement, and one of great value in all electrical investigations. The rod should be covered with a thick coating of shellac, and must be fastened by means of a cork, air-tight, into a glass flask previously dried by warming. These instruments are called electroscopes: when excited by the communication of a known kind of electricity, they show, by an increased or diminished divergence, the state of an electrified body brought into their neighbourhood (fig. 58).

One kind of electricity can no more be developed without the other than one kind of magnetism: the rubber and the body rubbed always assume opposite states, and the positive condition on the surface of a mass of matter is invariably accompanied by a negative state in all surrounding bodies.

Fig. 59.

The induction of magnetism in soft iron has its exact counterpart in electricity: a body already electrified disturbs or polarises the particles of all surrounding substances in the same manner and

and + on the outside. Becoming charged by the machine, and being discharged simultaneously with it by the knobs r, r', they strengthen the spark and increase its length.

The current of the machine is utilised by placing on the frame two brass uprights Q, Q′, with binding screws in which are copper wires, then by means of the handles K, K′, inclining the rods which support the knobs r, r', so as to bring them in contact with the uprights. The current being then directed by the wires, a battery can be quickly charged, water decomposed, a galvanometer deflected, and various other effects produced, as with the voltaic battery.

Very powerful electric excitation is produced by a jet of steam issuing at high pressure from a pipe provided with a nozzle of wood or metal, the effect being due, not to the pure steam itself, but to the friction of particles of condensed water against the inner surface of the exit-pipe. The steam is usually positive if the nozzle be constructed of wood or clean metal, but the slightest trace of oily matter produces a change of sign. The intensity of the charge increases, *cæteris paribus*, with the elastic force of the steam. A steam-boiler mounted on glass legs and provided with an exit-pipe, as above described, forms an electrical machine of very great power.

Condensers and Accumulators.—When the conductor of an electric machine is charged with electricity, it acts indirectly on all the surrounding conductors, in such a manner as to accumulate at their surfaces the electricity contrary to its own, producing the greatest effect on the conductor which is nearest to it and is in the best connection with the ground, whereby the electricity of the same kind as that of the machine may pass away. As the inducing electricity attracts the induced electricity of an opposite kind, so, on the other hand, is the former attracted by the latter. Hence, the electricity which the conductor receives from the machine must especially accumulate at that spot to which another good conductor of electricity is opposed. If a metal disc is in connection with the conductor of a machine, and if another similar disc, in good connection with the earth, is placed opposite to it, we have an arrangement by which tolerably large and good conducting surfaces can be brought close to one another, the positive condition of the first disc, as well as the negative condition of the other, being thereby increased in a very considerable degree. In this case, however, the limit is very soon reached, because the intervening air easily permits spark-discharge to take place through its substance; but with a solid insulating body, as glass or lac, this discharge takes place much less readily, even when the plate of insulating matter is very thin. It is on this principle that instruments for the *accumulation* of electricity depend, among which the Leyden jar is the most important.

A thin glass jar is coated on both sides with tinfoil, care being taken to leave several inches of the upper part uncovered (fig. 64); a wire, terminating in a metallic knob, communicates with the internal coating. When the outside of the jar is connected with

the earth, and the knob put in contact with the conductor of the machine, the inner and outer surfaces of the glass become respectively positive and negative, until a very great degree of intensity has been attained. On completing the connection between the two coatings by a metallic wire or rod, discharge occurs in the form of a very bright spark, accompanied by a loud snap: and if the human body be interposed in the circuit, the peculiar and disagreeable sensation of the electric shock is felt at the moment of its completion.

Fig. 64.

By enlarging the dimensions of the jar, or by connecting together a number of such jars in such a manner that all may be charged and discharged simultaneously, the power of the apparatus may be greatly augmented. By the discharge of such a combination—called an electric battery, thin wires of metal may be fused and dissipated; pieces of wood may be shattered; many combustible substances set on fire; and all the well-known effects of lightning exhibited upon a small scale. The circumstances of a thunderstorm indeed exactly resemble those of the charge and discharge of a coated plate or jar, the cloud and the earth representing the two coatings, and the intervening air the conducting body, or *dielectric*. The polarities of the opposed surfaces and of the insulating medium between them become raised by mutual induction, until violent disruptive discharge takes place through the air itself, or through any other bodies which may happen to be in the interval. When these are capable of conducting freely, the discharge is silent and harmless; but in other cases it often proves highly destructive. These dangerous effects may in a great measure be obviated by the use of lightning-rods attached to buildings. The masts of ships may be guarded in like manner by metal conductors. Sir W. Snow Harris devised a very ingenious plan for the purpose, which has been adopted, with complete success, in the Navy.

Fig. 65.

Condensing Electroscopes.—The delicacy of the gold-leaf electroscope may be greatly increased by laying on its cover a circular brass plate well polished; and on this another brass plate provided with an insulating handle and covered on its lower surface with copal varnish to prevent metallic contact between the two.

Hence they inferred that electricity is not developed by mere contact of dissimilar metals. Later experiments, however, made by Sir W. Thomson and by Messrs. Ayrton and Perry, with great care and extremely delicate apparatus, tend to confirm Volta's view, and to show that contact of metals does give rise to electric charge even when all extraneous causes of disturbance are removed. Moreover we may perhaps go so far as to say that, for the establishment of this point, no special experiments were required, the development of electric charge by the contact of dissimilar metals being sufficiently established by the phenomena of the thermo-electric circuit (p. 120), which in fact show that the development of electricity by such contact takes place *at all temperatures*, and in various degrees of intensity according to the temperature.

7. *Chemical Action.* Voltaic Electricity.—When two solid conducting bodies, generally metals, are immersed in a liquid which acts upon them unequally, the electric equilibrium is disturbed, the one acquiring the positive condition, and the other the negative. Thus, pieces of zinc and platinum put into dilute sulphuric acid, constitute an arrangement capable of generating electrical force: the zinc, which is the metal attacked, becomes negative; the platinum, which remains unaltered, assumes the positive condition; and on making a metallic communication in any way between the two plates, discharge ensues, evidenced by various electric phenomena, just as when the two surfaces of a coated and charged jar are put into connection. No sooner, however, has this occurred, than the disturbance is repeated; and as these successive charges and discharges take place through the fluid and metals with inconceivable rapidity, the result is an apparently continuous action, to which the term *electrical current* is given.

It is necessary, however, to guard against the idea, which this term naturally suggests, of an actual bodily transfer of something through the substance of the conductors, like water through a pipe: the real nature of these phenomena is not precisely known, but it probably consists in a movement or disturbance communicated from particle to particle throughout the whole chain. The word *current* is nevertheless convenient, and consecrated by long use; and with this caution, the very dangerous error of applying figurative language to describe an effect, and then seeking the nature of the effect from the common meaning of words, may be avoided.

The original cause of the electric disturbance under the circumstances here considered is still a matter of dispute. Some authorities, following Volta, consider that the electricity is developed by the contact of the dissimilar metals, which, as already observed, is a real cause of electric excitement; others again ascribe it solely to the chemical action between one of the metals and the liquid. In favour of the contact theory it may be urged that when pure zinc or zinc amalgamated with mercury is used, no action whatever is observable so long as the two metals remain unconnected, but as soon as they are made to touch, or are connected by a wire,

hydrogen begins to escape at the surface of the copper or platinum plate, and the entire circuit exhibits signs of electric action. On the other side it is alleged that so slight a force as that which has been shown to be developed by the mere contact of metals can scarcely give rise to the powerful effects which are produced by the arrangements now under consideration; moreover that the electric activity of the circuit appears to be always in proportion to the intensity of the chemical action between the metal and the liquid, and that the direction of the current produced depends altogether upon the manner in which that action takes place. Thus when a plate of iron and a plate of copper connected together are immersed in dilute sulphuric acid, the current of positive electricity is directed from the iron through the liquid to the copper, and back again through the connecting wire to the iron; but if the plates be taken out, washed with water, and then immersed in a solution of an alkaline sulphide, the current will take the contrary direction, viz., from the copper through the liquid to the iron,—that is to say, in both cases its direction is from the metal chemically acted upon, through the liquid to the unattacked metal. This question cannot with advantage be further discussed at present, but its consideration will be resumed in a subsequent part of the work, after the subject of chemical action in general has been more fully treated.

The intensity of the electrical excitement developed by a single pair of metals and a liquid is too feeble to be detected excepting by a delicate condensing electroscope; but, by arranging a number of such alternations in a connected series, in such a manner that the direction of the current shall be the same in each, the intensity may be very greatly exalted. The two instruments invented by Volta, called the pile and crown of cups, depend upon this principle.

To construct a Voltaic pile, we lay upon a plate of zinc a piece of cloth, rather smaller than itself, steeped in dilute acid, or any liquid capable of exerting chemical action upon the zinc; upon this is placed a plate of copper, silver, or platinum; then a second piece of zinc, another cloth, and a plate of inactive metal, until a pile of about twenty alternations has been built up. If the two terminal plates be now touched with wet hands, the sensation of the electrical shock will be experienced; but, unlike the momentary effect produced by the discharge of a jar, the sensation can be repeated at will by repeating the contact, and with a pile of one hundred such pairs, excited by dilute acid, it will be nearly insupportable. When such a pile is insulated, the two extremities exhibit strong positive and negative states; and when connection is made between them by wires armed with points of hard charcoal or plumbago, the discharge takes place in the form of a bright enduring spark or stream of fire.

Fig. 68.

dead frog when certain metals were made to touch the nerve and muscle at the same moment. It was Volta, however, who pointed out the electrical origin of these motions; and his name is very properly associated with the invaluable instrument his genius gave to science.

ELECTRO-MAGNETISM.

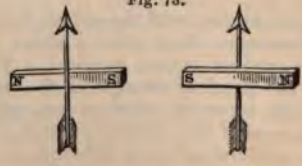
Although the fact that electricity is capable, under certain circumstances, both of inducing and of destroying magnetism, has long been known from the effects of lightning on the compass-needle and upon small steel articles, as knives and forks, to which polarity has suddenly been given by the stroke, it was not until 1819 that the laws of these phenomena were discovered by Oersted, of Copenhagen, and shortly afterwards fully developed by Ampère.

If a wire conveying an electrical current be brought near a magnetic needle, the latter will immediately alter its position, and assume a new one as nearly perpendicular to the wire as the mode of suspension and the magnetism of the earth will permit. When the wire, for example, is placed directly over the needle, and parallel to its length, while the current it carries travels from north to south, the needle is deflected from its ordinary direction, and the north pole driven to the eastward. When the current is reversed, the same pole deviates to an equal amount towards the west. Placing the wire below the needle instead of above produces the same effect as reversing the current.

Fig. 72.

The direction which the needle will assume when placed in any particular position relatively to the conducting wire may be determined by the following rule :—*Let the current be supposed to pass through a watch from the face to the back: the motion of the north pole will be in the direction of the hands.* Or, *let the observer imagine himself swimming in the direction of the current with his face towards the needle: the north pole of the needle will then be deflected towards his left hand.*

Fig. 73.

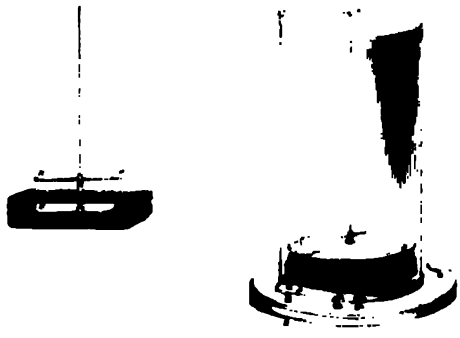


If reference is often required, a little piece of apparatus (fig. 73) may be used, consisting of a piece of pasteboard, or other suitable material, cut into the form of an arrow for indicating the current, crossed by a magnet having its poles marked, and arranged in the

[illegible] position with respect to the current. The latter is the case of the galvanoscope, consisting of placing the astatic magnet in the direction of the needle.

When the needle is subjected to the action of opposite directions, the one above and the one below, concur in their effects. The current of the wire covering the current is bent upon itself between the two portions as in the figure, the bending is repeated, a fresh portion of the wire is in the same manner upon the needle, and so on for as many as we please. A current, too feeble to produce any effect when a simple straight wire is employed, may be made by this contrivance to exert a powerful influence on the magnet. It is on this principle that instruments called *galvanometers*, *multipliers*, or *multipliers*, are constructed, which are used to indicate the existence of *voltaic* currents, but to measure the direction in which the current flows.

The sensibility of the instrument is increased by the use of a very long coil of wire and a very small needle. The two needles are of equal magnetic power, and are placed with their poles in the same direction, parallel, and with their poles opposite. They are suspended by a fibre of untwisted silk, with the lower one below and the upper one above it. The arrangement is called *astatic*, unaffected, or indifferent to the influence of the earth; and the needles, being thus unaffected by the earth's magnetism, are urged with the same force as they would be, all the actions of the current [illegible]



current. A divided circle is placed below the upper needle, by which the angular motion can be measured, and the whole is enclosed in a glass case, to shield the needles from the agitation of the air. The arrangement is shown in fig. 75.

The direction of the current which deflects the galvanometer-needle in a particular way is easily determined by the rules given on page 126, when we know the direction in which the wire is coiled round the frame. For this purpose it is necessary to distinguish between *right-handed* and *left-handed* coils or helices. Suppose the wire to be coiled round a cylinder beginning at the left hand; then if the turns in front of the cylinder proceed from below upwards, as in fig. 76, the coil is left-handed; if, on the contrary, they proceed in front from above downwards, as in fig. 77, the coil is right-handed.

Fig. 76.

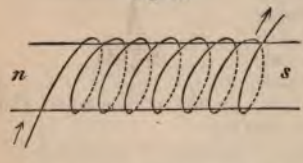
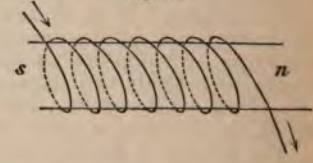


Fig. 77.



A magnetic needle placed with its centre in the axis of such a coil turns its north or south pole towards the end of the coil at which the current enters, according as the coil is left or right-handed.

The direction given to the needle is the same whether the coil is elongated, as in the above figures, or compressed, as in the galvanometer. As, however, in the galvanometer, when complete, it is not easy to see whether the coil is left or right-handed, it is best to determine by experiment, once for all, the direction taken by the needle when the current enters at one particular end of the coil.

Action of the Magnet on the Electric Current.—The action between the current and the magnet is mutual, so that if the conductor conveying the current is free to move, it is deflected in the direction opposite to that which the magnet takes under its influence; in short, if the magnet and conducting wire are both free to move, they place themselves at right angles to each other, the magnet moving in the manner indicated at page 126, and the wire in the opposite direction.

The action of the magnet on the current may be shown by means of Ampère's apparatus (fig. 78). On holding a bar-magnet below the rectangular wire, and parallel to its lower horizontal arm, the wire turns round and places itself at right angles to the magnet, the position of equilibrium being determined by the rule just alluded to.

A simpler apparatus for this purpose is De la Rive's floating battery, which consists of a pair of zinc and copper plates, contained

in a wide glass tube attached to a cork float, and connected together by a rectangular wire, or a flat coil, or elongated helix of covered wire (fig. 79).

Fig. 78.

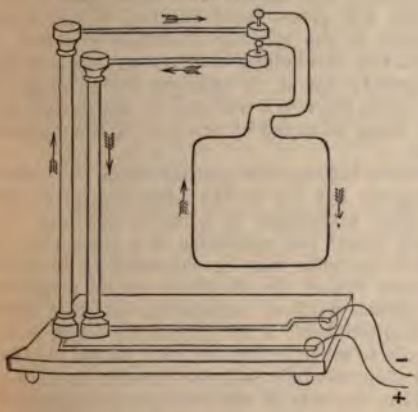
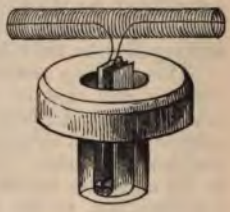


Fig. 79.



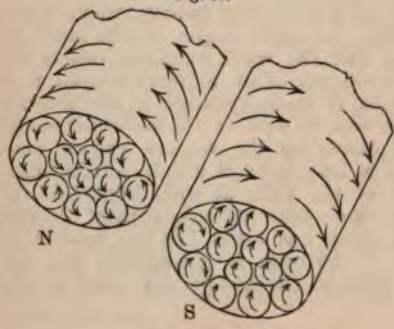
A movable electric current is deflected by the earth's magnetism in the same way as by an ordinary magnet. Thus the rectangular wire of Ampère's apparatus, or of a floating battery, when left to itself, will take up a position at right angles to the magnetic meridian; and remembering that the north magnetic pole of the earth is analogous to the south pole of an ordinary magnet, it is easy to see that, in the position of stable equilibrium, the direction of the current will be from east to west in the lower horizontal branch, and from below upwards on the western vertical side. If the wire has the form of a long helix, it will, in like manner, place itself with the turns of the helix at right angles to the magnetic meridian, and therefore with its axis parallel to that meridian, the ends pointing north and south, just like those of an ordinary magnetic needle. If the helix is left-handed, the end connected with the copper plate of the battery will point to the north.

Mutual Action of Electric Currents.—If a conducting wire connecting the poles of a voltaic battery be brought near the movable wire of Ampère's apparatus, or the wire of a floating battery, the movable wire will be attracted or repelled according to the relative direction of the two currents, the general law of the action being that, *electric currents moving in parallel lines attract one another if they move in the same direction, and repel one another if they move in opposite directions.* From this it is easy to see that if

a helix connecting the two poles of a battery be brought near the helix of a floating battery, and if the two helices are similar,—that is, both right or both left-handed,—their similar ends, *i.e.*, those by which the current enters or leaves the helix, will repel each other, and their dissimilar ends will attract each other, and consequently the movable helix will place itself parallel to the fixed helix with its poles or ends in the contrary direction to those of the fixed helix. In short, the two helices will act on one another exactly like two bar magnets; and if an ordinary bar magnet be substituted for the fixed helix, the effect will still be the same, each end of the movable helix being attracted by one pole of the magnet, and repelled by the other.

This striking resemblance between the mutual action of electric currents and that of magnets has led to the idea, suggested and developed by Ampère, that magnetism is actually produced by electric currents circulating round the molecules of a magnet all in the same direction. These currents may be supposed to pre-exist in all magnetic bodies, even before the development of magnetic polarity, but to be disposed without regularity, so that they neutralise each other. Magnetisation is the process by which these molecular currents are made to move in one direction, those situated at the surface yielding, as their resultant, a finite current circulating round the magnet, while the currents in the interior are neutralised by those in the next external layer, the contiguous portions of which move in a direction opposite to their own. The resultant action of all these molecular currents is equivalent to that of a number of currents circulating round the magnet in planes perpendicular to its axis (fig. 80); and from what has been said about the mutual action of magnets and helices traversed by electric currents, it is easy to see that, on looking along the axis of a magnet with its *south* pole towards the observer, the current moves in the direction of the hands of a watch, that is, upwards on the left side, and downwards on the right.

Fig. 80.



ELECTRO-DYNAMIC INDUCTION.

1. *Magnetisation by the Current.*—When an electro-current is passed through a wire placed at right angles to a bar of iron or steel the bar acquires magnetic polarity, temporary in the case of

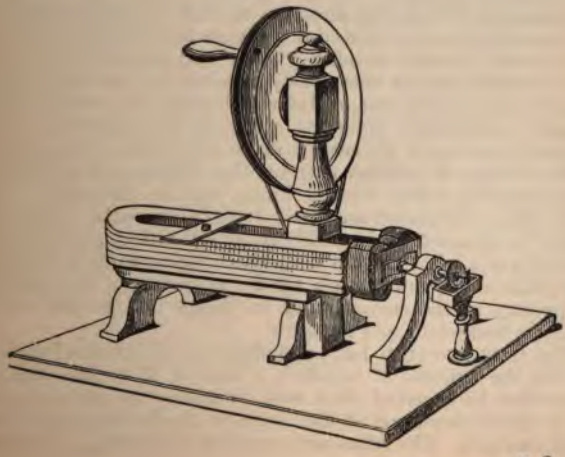
soft iron, permanent in the case of hard iron or steel, the position of the poles being determined by the direction of the current, according to the laws already explained.

This effect is prodigiously increased by coiling the conducting wire in a helix round the bar. A piece of soft iron worked into the form of a horseshoe (fig. 81), and surrounded by a coil of wire covered with silk or cotton for the purpose of insulation, furnishes an excellent illustration of the inductive energy of the current in this respect: when the ends of the wire are put into communication with a small voltaic battery of a single pair of plates, the iron instantly becomes so highly magnetic as to be capable of sustaining a very heavy weight.

Fig. 81.

2. *Induction of Electric Currents by the action of Magnets, and of other Electric Currents.*—If the two extremities of the coil of the electro-magnet above described be connected with a galvanoscope, and the iron magnetised by the application of a permanent steel horse-shoe magnet to the ends of the bar, a momentary current will be developed in the wire, and pointed out by the movement of the needle. It lasts but a single instant, the needle, after a few oscillations, returning to a state of rest. On removing the magnet, whereby the polarity of the iron is at once destroyed, a second current or wave will become apparent, but in

Fig. 82.



the opposite direction to that of the first. By employing a very powerful steel magnet, surrounding its iron keeper or armature with a very long coil of wire, and then making the armature itself rotate in front of the faces of the magnet, so that its induced polarity shall be rapidly reversed, magneto-electric currents may be produced, of such intensity as to give bright sparks and most powerful shocks, and exhibit all the phenomena of voltaic electricity. Fig. 82 represents a powerful arrangement of this kind.

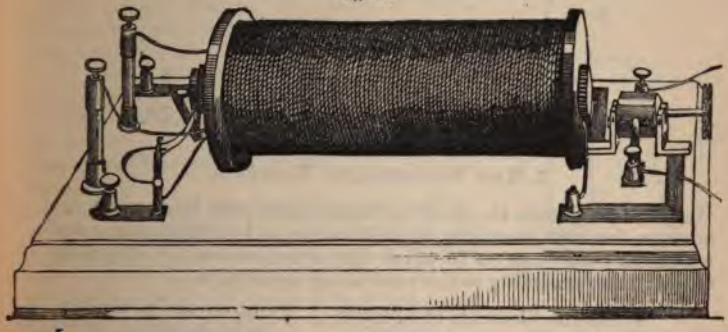
By using electro-magnets instead of permanent steel magnets, and rotating an armature between them by steam-power, very powerful machines, called "Dynamo-electric machines," are constructed, which are now extensively used for electric lighting and other applications of electricity. The light is produced by passing a strong current between two cylinders of hard carbon, whereby an arch of light of almost unendurable brilliancy is obtained—this is called the "Arc Light"—or by sending a current through a thin filament of carbon (prepared by heating cotton-thread or bamboo-fibre in a close vessel) placed in a glass vessel from which the air is exhausted by a Sprengel pump (p. 27), so that the carbon is made to glow without burning. This is called the "Incandescent Light." These, however, are matters the further discussion of which would be foreign to the object of this work. For information respecting them see Silvanus Thompson's "Elementary Lessons on Electricity and Magnetism," pp. 362—378.

Induction-coils.—When two covered wires are twisted together or laid side by side for some distance, and a current is transmitted through the one, a momentary electrical wave will be induced in the other in the reverse direction; and on breaking connection with the battery, a second single wave will become evident by the aid of the galvanoscope, in the same direction as that of the primary current. The same effects are produced if the wires are twisted, one above the other, round a hollow wooden cylinder, and the intensity of the induced currents may be enormously increased by inserting within the cylinder a bar of soft iron, or better, a bundle of iron wires, whereby magnetic and electric induction are made to cooperate. The more frequently contact is alternately made and broken, the greater will be the number of induced currents that follow each other, and the more powerful, within certain limits, will be the action. Instruments thus constructed are called induction-coils. The contact-breaker or commutator is usually made self-acting, an ordinary form consisting of a piece of thin steel which makes contact with a platinum point, and is drawn back by the attraction of the iron core on the passing of the current, and so makes and breaks circuit by vibrating backwards and forwards.

The most powerful form of induction-coil is that of Ruhmkorff (fig. 83), the cylinder of which is a foot or 18 inches long, and is surrounded by a coil of thick wire to convey the inducing current, and a much longer coil of thin wire for the development of the induced currents. The wires are insulated with resin. The direction

of the battery-current can be changed at pleasure by a commutator, by which the battery-poles are connected through the ends of the

Fig. 83.



axis of a small ivory or ebonite cylinder to two cheeks of brass, which can be turned so as to place them either way in contact with two vertical springs, which are joined to the ends of the primary coil. This apparatus forms a very powerful electric machine, capable of yielding electricity of very high intensity, giving long sparks, and shocks of unendurable force. It is capable also of firing gunpowder and other inflammable materials, and has been used for exploding charges of gunpowder and other inflammable substances for mining, engineering, and military purposes. It is also frequently used in the chemical laboratory for firing gaseous mixtures.

PART II.

CHEMISTRY OF ELEMENTARY BODIES.

1. The Non-metallic Elements.

We shall commence the study of these bodies with hydrogen, and arrange the rest according to the number of hydrogen-atoms with which they can unite, or to which they are equivalent (p. 13), designating them, according to this combining capacity, as :—

Univalent Elements or Monads .	H, Cl, Br, I, F.
Bivalent Elements or Dyads . .	O, S, Se, Te.
Trivalent Elements or Triads . .	N, P, As, B.*
Quadrivalent Elements or Tetrads .	Si, C.

HYDROGEN.

Symbol, H. Atomic weight, 1. Density, 1.

Hydrogen does not occur naturally in the free state, but may be obtained by deoxidation of water, of which it is a component.†

If a tube of iron or porcelain, containing a quantity of filings or turnings of iron, be fixed across a furnace, and its middle portion be made red-hot, and then the vapour of water passed over the heated metal, a large quantity of permanent gas will be disengaged from the tube, and the iron will be converted into oxide, and acquire an increase in weight. The gas is hydrogen; it may be collected over water and examined.

Hydrogen is, however, more easily obtained by decomposing hydrochloric or dilute sulphuric acid with zinc, the metal then displacing the hydrogen in the manner already explained (p. 12).

The simplest method of preparing the gas is the following :— A wide-necked bottle is fitted with a sound cork, perforated by two holes for the reception of a small tube-funnel reaching nearly

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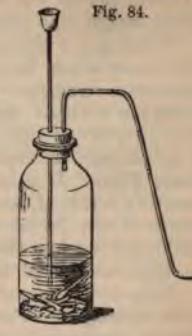
* Boron is not known to combine with hydrogen; but it is placed in this group because it unites with three atoms of other univalent elements and radicles, forming, for example, the compounds BCl_3, $B(CH_3)_3$, $B(C_2H_5)_3$.

† Hence the name, from ὕδωρ, water, and γεν, a root signifying production.

to the bottom of the bottle, and a piece of bent glass* tube to convey away the disengaged gas. Granulated zinc, or scraps of the malleable metal are put into the bottle, together with a little water, and sulphuric acid slowly added by the funnel, the point of which should dip into the liquid. The evolution of gas is easily regulated by the supply of acid; and when enough has been discharged to expel the air of the vessel, it may be collected over water in a jar, or passed into a gas-holder. In the absence of zinc, filings of iron or small nails may be used, but with less advantage.

Fig. 84.



Hydrogen is colourless, tasteless, and inodorous when quite pure. To obtain it in this condition, it must be prepared from the purest zinc that can be obtained, and passed in succession through solutions of potash and silver nitrate. When prepared from commercial zinc, it has a slight smell, due to impurity, and when iron has been used, the odour is very strong and disagreeable. It is inflammable, and burns, when kindled, with a pale yellowish flame, evolving much heat, but very little light. The product of the combustion is water. Hydrogen is very slightly soluble in water. Although destitute of poisonous properties, it is incapable of sustaining life. By strong pressure and exposure to a very low temperature it may be liquefied and even solidified (p. 63).

Fig. 85.

Hydrogen is the lightest substance known; Dumas and Boussingault place its density between 0·0691 and 0·0695, referred to that of air as unity. The weight of a litre of hydrogen at 0° C., and

* A little practice will soon enable the pupil to construct and arrange a variety of useful forms of apparatus, in which bottles, and other articles always at hand, are made to supersede more costly instruments. Glass tube, purchased by weight of the maker, may be cut by scratching with a file, and then applying a little force with both hands. Glass may be softened and bent, when of small dimensions, by the flame of a spirit-lamp, or a candle, or, better, by a gas jet. Corks may be perforated by a heated wire, and the hole rendered smooth and cylindrical by a round file; or the ingenious cork-borer of Dr. Mohr, now to be had of all instrument makers, may be used instead. Lastly, in the event of bad fitting, or unsoundness in the cork itself, a little yellow wax melted over the surface, or even a little grease applied with the finger, renders it sound and air-tight, when not exposed to heat.

under a barometric pressure of 0·760 meter, is 0·089578 gram; consequently a gram of hydrogen occupies a space of 11·16345 litres.* At 15·5° C. (60° F.), and 30 inches barometric pressure, 100 cubic inches weigh 2·14 grains.

When a gas is much lighter or much heavier than atmospheric air, it may often be collected and examined without the aid of the pneumatic trough. A bottle or narrow jar may be filled with hydrogen without much admixture of air, by inverting it over the extremity of an upright tube delivering the gas. In a short time, if the supply be copious, the air will be wholly displaced, and the vessel filled. It may now be removed, the vertical position being carefully retained, and closed by a stopper or a glass plate. If the mouth of the jar be wide, it must be partially closed by a piece of cardboard during the operation. This method of collecting gases by displacement is often extremely useful.

Soap-bubbles and small collodion balloons ascend when filled with hydrogen. Caoutchouc balloons are filled and expanded by forcing hydrogen into them with a syringe. Hydrogen was formerly used also for filling air-balloons, being made for the purpose on the spot from zinc or iron and dilute sulphuric acid; but its use is now superseded by that of coal-gas, which may be made very light by employing a high temperature in the manufacture. Although far inferior to pure hydrogen in buoyant power, it is found in practice to possess advantages over that substance, while its greater density is easily compensated by increasing the size of the balloon.

Diffusion of Gases.—There is a very remarkable property possessed by gases and vapours in general, which is seen in a high degree of intensity in the case of hydrogen; that is what is called diffusive power. If two bottles containing gases which do not act chemically upon each other at common temperatures be connected by a narrow tube and left for some time, the gases after a certain time, depending much upon the narrowness of the tube and its length, will be found uniformly mixed, even though they differ greatly in density, and the system has been arranged in a vertical position with the heavier gas downwards. Oxygen and hydrogen can thus be made to mix, in a few hours, against the action of gravity, through a tube a yard long, and not more than one quarter of an inch in diameter: and the same is true of all other gases which do not act directly upon each other.

If a vessel be divided into two portions by a diaphragm or partition of porous earthenware or dry plaster of Paris, and each half of it filled with a different gas, diffusion will immediately commence through the pores of the dividing substance, and will continue until

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* As a near approximation, it may be remembered that a litre of hydrogen weighs 0·09 gram, or 9 centigrams, and a gram of hydrogen occupies 11·2 litres.

perfect mixture has taken place. All gases, however, do not permeate the same porous body, or, in other words, do not pass through narrow orifices, with the same degree of facility. Graham, to whom we are indebted for a very valuable investigation of this interesting subject, established the existence of a very simple relation between the rapidity of diffusion and the density of the gas, which is expressed by saying that the diffusive power varies inversely as the square root of the density of the gas itself. Thus, in the experiment supposed, if one-half of the vessel be filled with hydrogen and the other half with oxygen, the two gases will penetrate the diaphragm at very different rates, four cubic inches of hydrogen passing into the oxygen side, while one cubic inch of oxygen travels in the opposite direction. The densities of the two gases are to each other in the proportion of 1 to 16; their relative rates of diffusion are inversely as the square roots of these numbers, *i.e.*, as 4 to 1.

In order, however, that this law may be accurately observed, it is necessary that the porous plate be very thin; with plates of stucco an inch thick or more, which really consist of a congeries of long capillary tubes, a different law of diffusion is observed.* An excellent material for diffusion experiments is the artificially compressed graphite of Mr. Brockedon, of the quality used for making writing pencils. It may be reduced by cutting and grinding to the thickness of a wafer, but still retains considerable tenacity. The pores of this substance appear to be so small as entirely to prevent the transmission of gases in mass, so that, to use the language of Mr. Graham, it acts like a molecular sieve, allowing only molecules to pass through.

The simplest and most striking method of exhibiting the phenomenon of diffusion is by the use of Graham's diffusion-tube (fig. 86). This is merely a piece of wide glass tube ten or twelve inches long, having one of its extremities closed by a plate of plaster of Paris about half an inch thick, and well dried. When the tube is filled by displacement with hydrogen, and then set upright in a glass of water, the level of the liquid rises in the tube so rapidly, that its movement is apparent to the eye, and speedily attains a height of several inches above the water in the glass. The gas is actually rarefied by its superior diffusive power over that of the external air.

Fig. 86.

It is impossible to over-estimate the importance in the economy of Nature of this law affecting the constitution of gaseous bodies; it is the principal means by which the atmosphere is preserved in a uniform state, and the accumulation of poisonous

* See Bunsen's Gasometry, p. 203; Graham's Elements of Chemistry, 2d ed. ii. 624; Watts's Dictionary of Chemistry, ii. 815.

and effusion are essentially different in their nature, the effusive movement affecting masses of a gas, whereas the diffusive movement affects only molecules; and a gas is usually carried by the former kind of impulse with a velocity many thousand times greater than by the latter. Mixed gases are effused at the same rates as one gas of the actual density of the mixture: and no separation of the gases occurs, as in *diffusion* into a vacuum.

The law of effusion just stated is true only under the condition that the gas shall pass through a minute aperture in a very thin plate. If the plate be thicker, so that the aperture becomes a tube, very different rates of efflux are observed; and when the capillary tube becomes considerably elongated, so that its length exceeds its diameter at least 400 times, the rates of flow of different gases into a vacuum again assume a constant ratio to each other, following, however, a law totally distinct from that of effusion. The chief general results observed with relation to this phenomenon of "Capillary Transpiration" are as follows:—

1. The rate of transpiration of the same gas increases, *cæteris paribus*, directly as the pressure: in other words, equal volumes of gas at different densities require times inversely proportional to their densities. 2. With tubes of equal diameter, the volume transpired in equal times is inversely as the length of the tube. 3. As the temperature rises, the transpiration of equal volumes becomes slower. 4. The rates of transpiration of different gases bear a constant relation to each other, totally independent of their densities, or, indeed, of any known property of the gases. Equal *weights* of oxygen, nitrogen, and carbon monoxide are transpired in equal times; so likewise are equal weights of nitrogen, nitrogen dioxide, and carbon monoxide; and of hydrogen chloride, carbon dioxide, and nitrogen monoxide.*

CHLORINE.

Symbol, Cl. Atomic weight, 35·37. Density, 35·37.

This substance is a member of a very important natural group, containing also iodine, bromine, and fluorine. So great a degree of resemblance exists between these bodies in all their chemical relations, especially between chlorine, bromine, and iodine, that the history of one will almost serve, with a few alterations, for that of the rest. On account of the occurrence of chlorine, bromine, and iodine in sea-water, the elements of this group are called halogen-elements, and their metallic compounds, haloïd compounds.†

Chlorine is a very abundant substance: in common salt it exists

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* Graham, Phil. Trans, 1846, p. 591, and 1849, p. 349; also Elements of Chemistry, 2d ed., i. 82.

† From ἁλς, the sea.

in combination with sodium. It is most easily prepared by pouring strong hydrochloric acid upon finely powdered black oxide of manganese (MnO_2) contained in a retort or flask (fig. 87), and applying a gentle heat; the chlorine then passes over in the form of a heavy yellow gas, which may be collected over warm water, or by displacement: the mercurial trough cannot be employed, as chlorine rapidly acts upon the metal, and becomes absorbed.

The reaction consists in an interchange between the two atoms of oxygen of the manganese dioxide and 4 atoms of chlorine from the hydrochloric acid, the oxygen uniting with the hydrogen to form water, while, of the chlorine, one-half unites with the manganese, forming a chloride, $MnCl_2$, and the other half is given off as gas:

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2.$$

The same process is used for the preparation of chlorine on the manufacturing scale, the hydrochloric acid which is evolved in large quantities by heating common salt with sulphuric acid, in Leblanc's soda-process, being utilised for the purpose.

Fig. 87.

The waste-liquor obtained in the chlorine manufacture consists of an impure solution of manganous chloride, $MnCl_2$, from which the manganese may be separated by an alkali in the form of manganous oxide, MnO. But to render the manganese thus precipitated again available for the production of chlorine, it must first be brought to the state of dioxide, and this may be effected by mixing the manganese liquor with an excess of hot milk of lime, or magnesia, and blowing hot air through the mixture. By this means, a compound of manganese dioxide with lime or magnesia, *e.g.*, CaO,MnO_2, or $CaMnO_3$, called calcium or magnesium manganite, is formed, which, when heated with hydrochloric acid, gives off chlorine in the manner above described. This is Weldon's process for the regeneration of manganese, which is now largely used both in England and on the Continent.

A process for the separation of chlorine from hydrochloric acid, without the use of any manganese compound, was introduced by the late Mr. H. Deacon. It consists in passing a mixture of hydrochloric acid gas and oxygen, or air, over cupric sulphate or other cupric salt heated to 370–400° C. (698—752° F.), the hydrochloric acid being then decomposed, its hydrogen combining with the oxygen, and the chlorine being set free. The best way of conducting the process is to pass the mixed gases over pieces of brick soaked in solution of cupric sulphate and dried. The action of the copper salt is not well understood, but appears to belong to that

class of phenomena called catalytic or contact actions. Other metallic salts act in a similar way, but less completely.

Chlorine is a yellow gaseous body, of intolerably suffocating properties, producing very violent cough and irritation when inhaled, even in exceedingly small quantity. It is soluble to a considerable extent in water, that liquid absorbing at 15·5° about twice its volume, and acquiring the colour and odour of the gas. When this solution is exposed to light, it is slowly changed, by decomposition of water, into hydrochloric acid, the oxygen being at the same time liberated. When moist chlorine gas is exposed to a cold of 0°, yellow crystals are formed, which consist of a definite compound of chlorine and water containing 35·5 parts of the former to 90 of the latter.

Chlorine has a specific gravity of 2·45; a litre of it weighs 3·167 grams; exposed to a pressure of about four atmospheres, it condenses to a yellow limpid liquid.

Chlorine has but little attraction for oxygen, its energies being principally exerted towards hydrogen and the metals. A lighted taper plunged into the gas continues to burn with a dull-red light, and emits a large quantity of smoke, the hydrogen of the wax being alone consumed, and the carbon separated. If a piece of paper be wetted with oil of turpentine, and thrust into a bottle filled with chlorine, the chemical action of the latter upon the hydrogen is so violent as to cause inflammation accompanied by a copious deposit of soot. Chlorine, may, by indirect means, be made to combine with carbon; but this combination never occurs under the circumstances just described.

Phosphorus takes fire spontaneously in chlorine, burning with a pale and feebly luminous flame. Several of the metals, as copper-leaf, powdered antimony, and arsenic, undergo combustion in the same manner. A mixture of equal measures of chlorine and hydrogen explodes with violence on the passage of an electric spark, or on the application of a lighted taper, hydrochloric acid gas being formed. Such a mixture may be kept in the dark for any length of time without change, but on exposing it to diffused daylight, the two gases slowly unite, while the direct rays of the sun induce instantaneous explosion.

The most characteristic property of chlorine is its bleaching power; the most stable organic colouring principles are instantly decomposed and destroyed by it: indigo, for example, which resists the action of strong oil of vitriol, is converted by chlorine into a brownish substance, to which the blue colour cannot be restored. The presence of water is essential to these changes, for the gas in a state of perfect dryness is incapable even of affecting litmus.

Chlorine is largely used in the arts for bleaching linen and cotton goods, rags for the manufacture of paper, &c. For these purposes, it is employed, sometimes in the state of gas, sometimes in that of aqueous solution, but more frequently in combination with lime, forming the substance called bleaching-powder. It is also one of the best and most potent substances that can be used for the

purpose of disinfection, but its employment requires care. Bleaching-powder mixed with water, and exposed in shallow vessels, is slowly decomposed by the carbonic acid of the air, and the chlorine is evolved: if a more rapid disengagement be wished, a little acid may be added. In the absence of bleaching-powder, either of the methods for the production of the gas described may be had recourse to, always taking care to avoid an excess of acid.

Hydrogen Chloride, or **Hydrochloric Acid**, HCl; also called *Chlorhydric* and *Muriatic Acid*.—This substance, in the state of solution in water, has long been known. The gas is easily prepared by heating, in a flask fitted with a cork and bent tube, a mixture of common salt and oil of vitriol diluted with a small quantity of water; it must be collected by displacement, or over mercury. It is a colourless gas, which fumes strongly in the air from condensing the atmospheric moisture; it has an acid, suffocating odour, but is much less offensive than chlorine. Exposed to a pressure of 40 atmospheres, it liquefies.

Hydrochloric acid gas has, according to experiment, a density of 1·278 compared with air, or 18·44 compared with hydrogen as unity, the calculated number being $\frac{35{\cdot}37 + 1}{2} = 18{\cdot}185$. It is exceedingly soluble in water, that liquid taking up, at the temperature of the air, about 418 times its bulk. The gas and solution are powerfully acid.

The action of sulphuric acid on common salt, or any analogous substance, is explained by the equation,

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The composition of hydrochloric acid may be determined by synthesis: when a measure of chlorine and a measure of hydrogen are fired by the electric spark, two measures of hydrochloric acid gas result, the combination being unattended by change of volume. By weight the gas contains 35·37 parts of chlorine and 1 part of hydrogen.

Solution of hydrochloric acid, the liquid acid of commerce, is a very important preparation, and of extensive use in chemical pursuits: it is best prepared by the following arrangement:—

A large glass flask, containing a quantity of common salt, is fitted with a cork and bent tube, in the manner represented in fig. 88: this tube passes through and below a second tube into a wide-necked bottle containing a little water, into which the open tube dips. A bent tube is adapted to another hole in the cork of the wash-bottle, so as to convey the purified gas into a quantity of distilled water, by which it is instantly absorbed: the joints are made air-tight by melting a little yellow wax over the corks. A quantity of sulphuric acid, about equal in weight to the salt, is then slowly introduced by the funnel; the disengaged gas is at first wholly absorbed by the water in the wash-bottle, but when this becomes saturated, it passes into

boils above 200°, the vapour having an exceedingly beautiful violet colour.* It is slowly volatile also at common temperatures, and exhales an odour much resembling that of chlorine. The density of the vapour is, by experiment, 8·716 compared with air, or 125·8 compared with hydrogen, the theoretical density being 126·53. Iodine requires for solution about 7000 parts of water, to which nevertheless it imparts a brown colour; in alcohol it is much more freely soluble. Solutions of hydriodic acid and the iodides of the alkali-metals also dissolve it in large quantity: these solutions are not decomposed by water, which is the case with the alcoholic tincture.

Iodine stains the skin, but not permanently; it has a very energetic action upon the animal system, and is much used in medicine.

One of the most characteristic properties of iodine is the production of a splendid blue colour by contact with starch. The iodine for this purpose must be free or uncombined. It is easy, however, to make the test available for the purpose of recognising the presence of the element in question when a soluble iodide is suspected; it is only necessary to add a very small quantity of chlorine-water, when the iodine, being displaced from combination, becomes capable of acting upon the starch.

Hydrogen Iodide, or **Hydriodic Acid**, HI.—The simplest process for preparing hydriodic acid gas is to introduce into a test-tube a little iodine, then a small quantity of roughly-powdered glass moistened with water, upon this a few fragments of phosphorus, and lastly more glass, this order of iodine, glass, phosphorus, glass, being repeated until the tube is half or two-thirds filled. A cork and narrow bent tube are then fitted, and gentle heat is applied. The gas is best collected by displacement of air. The process depends on the formation of an iodide of phosphorus and its subsequent decomposition by water, whereby hydrogen phosphite, or phosphorous acid, H_3PO_3, and hydrogen iodide are produced: $P_2 + I_6 + 6H_2O = 6HI + 2H_3PO_3$. The glass merely serves to moderate the violence of the action, and may be dispensed with if amorphous phosphorus be used.

Fig. 90.

Hydriodic acid gas greatly resembles the corresponding chlorine compound; it is colourless, and highly acid, fumes in the air, and

* Whence the name, from *ἰώδης*, violet-coloured.

is very soluble in water. Its density is 4·3737 compared with air, or 63·13 compared with hydrogen; theoretic density 63·765. By weight, it is composed of 126·53 parts iodine and 1 part hydrogen; and by measure of equal volumes of iodine vapour and hydrogen united without condensation.

Solution of hydriodic acid may be prepared by a process much less troublesome than the above. Iodine in fine powder is suspended in water, and a stream of washed hydrogen sulphide is passed through the mixture; sulphur is then deposited, and the iodine is converted into hydriodic acid. When the liquid has become colourless, it is heated, to expel the excess of hydrogen sulphide, and filtered. The solution cannot be kept long, especially if it be concentrated; the oxygen of the air gradually decomposes the hydriodic acid, and iodine is set free, which, dissolving in the remainder, colours it brown.

Iodine and Chlorine.—These bodies unite directly, forming a monochloride and a trichloride. The *monochloride*, ICl, is obtained by passing dry chlorine gas over iodine till the whole is liquefied, but no longer; also by distilling iodine with potassium chlorate, oxygen being then evolved, the monochloride distilling over, and a mixture of chloride, iodate, and perchlorate of potassium remaining behind.

$$I_2 + 3KClO_3 = O_2 + ICl + KCl + KIO_3 + KClO_4.$$

Iodine monochloride is a reddish-brown oily liquid, having a suffocating odour and astringent taste; soluble in alcohol and ether; decomposed by water, with formation of hydrochloric and iodic acids, and separation of iodine. It sometimes solidifies in yellow needles. Sulphurous acid and hydrogen sulphide decompose it, with separation of iodine; with aqueous solutions of alkalis, it yields a chloride and an iodate, together with free iodine; thus, with potash—

$$5ICl + 6KHO = 5KCl + KIO_3 + 3H_2O + I_4.$$

The *trichloride*, ICl_3, is produced by treating iodine at a gentle heat with chlorine in excess. It crystallises in orange-yellow needles; melts at 20° to 25°, giving off chlorine, which it reabsorbs on cooling; acts on most other substances like the monochloride.

In contact with a small quantity of water it is partly resolved into an insoluble yellowish body (probably a mixture of the trichloride with iodic oxide), and a solution containing hydrochloric acid and the monochloride—

$$4ICl_3 + 5H_2O = 10HCl + I_2O_5 + 2ICl.$$

A large quantity of water dissolves it, probably without decomposition, or perhaps as a mixture of hydrochloric and iodic acids containing free iodine—

$$5ICl_3 + 9H_2O = 15HCl + 3HIO_3 + I_2.$$

The *tetrachloride*, ICl_4, produced by spontaneous decomposition of the monochloride, $4ICl = ICl_4 + I_3$, crystallises in red octohedrons.

Iodine and Bromine.—Iodine unites with bromine, forming a volatile crystalline compound, probably IBr, and a dark liquid, possibly IBr_3.

FLUORINE.

Symbol, F. Atomic weight, 19.

THIS element exists in considerable quantity, in combination with calcium, forming the mineral called fluorspar, which crystallises in fine cubes of various colours. Fluorine occurs also in small quantity as a constituent of bones and other animal substances. Its intense affinities for metals and for silicon, which is a constituent of glass, have hitherto baffled all attempts to isolate it in a state fit for examination, but Dr. Brauner,* by heating cerium tetrafluoride, has obtained a lower fluoride of cerium, together with a gas smelling like chlorine or hypochlorous oxide. The reaction is probably $CeF_4 = CeF_3 + F$. Anhydrous tetrafluoride of lead is also decomposed by heat, yielding the difluoride, and a gas smelling like chlorine.

Hydrogen Fluoride, or **Hydrofluoric Acid**, HF.—When powdered calcium fluoride is heated with concentrated sulphuric acid in a retort of platinum or lead connected with a carefully cooled receiver of the same metal, a very volatile colourless liquid is obtained, which emits copious white and highly suffocating fumes in the air. This is the anhydrous acid, not however quite pure. It may be obtained in a state of perfect purity by distilling hydrogen-potassium fluoride, HF,KF, to redness in a platinum vessel. As thus prepared, it is at ordinary temperatures a colourless, transparent, mobile liquid, having a specific gravity of 0·9879 at 12·8°, extremely volatile, boiling at 19·4°, fuming densely at ordinary temperatures, and absorbing water greedily from the air.

Gore, by measuring the volume of hydrogen required to combine with the fluorine contained in a known weight of fluorspar, found that 1 volume of hydrogen yields 2 volumes of gaseous hydrogen fluoride containing 19 parts by weight of fluorine to 1 part of hydrogen. The density of the gaseous acid is 10 times that of hydrogen.

When hydrofluoric acid is put into water, it unites with the latter with great violence; the dilute solution attacks glass with

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* Journal of the Chemical Society, xlii, 8.

great facility. The concentrated acid, dropped upon the skin, occasions deep malignant ulcers, so that great care is requisite in its management.

In a diluted state, this acid is occasionally used in the analysis of siliceous minerals, when alkali is to be estimated; it is employed also for etching on glass, for which purpose the acid may be prepared in vessels of lead, that metal being but slowly attacked under these circumstances. The vapour of the acid is also very advantageously applied to the same purpose in the following manner:— The glass to be engraved is coated with etching-ground or wax, and the design traced in the usual way with a pointed instrument. A shallow basin, made by beating up a piece of sheet-lead, is then prepared, a little powdered fluorspar placed in it, and enough sulphuric acid added to form with the latter a thin paste. The glass is placed upon the basin, with the waxed side downwards, and gentle heat applied beneath, which speedily disengages the vapour of hydrofluoric acid. In a very few minutes the operation is complete; the glass is then removed, and cleaned by a little warm oil of turpentine. When the experiment is successful, the lines are very clean and smooth.

OXYGEN.

Symbol O. Atomic weight, 15·96. Density, 15·96.

Oxygen was discovered in the year 1774, by Scheele, in Sweden, and Priestley, in England, independently of each other, and described under the terms *empyreal air* and *dephlogisticated air*. The name oxygen* was given to it by Lavoisier some time afterwards. Oxygen exists in a free and uncombined state in the atmosphere, mixed with another gaseous body, nitrogen. No very good direct means exist, however, for separating it from the latter; and, accordingly, it is always obtained for purposes of experiment by decomposing certain metallic oxides.

The red oxide of mercury, or *red precipitate* of the old writers, may be employed for this purpose. In this substance the attraction which holds together the mercury and the oxygen is so feeble, that simple exposure to heat suffices to bring about decomposition.

The mode of conducting the decomposition and collecting the evolved gas has already been noticed (p. 29). The experiment there described is, however, instructive rather as an instance of the resolution by simple means of a compound body into its constituents, than as a means of obtaining oxygen gas. A better and more economical method is to expose to heat in a retort, or flask furnished with a bent tube, a portion of the salt called potassium chlorate.

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* From ὀξὺ, acid, and γεν, a root signifying production.

A common Florence flask serves perfectly well, the heat of the spirit-lamp being sufficient. The salt melts and decomposes with ebullition, yielding a very large quantity of oxygen gas, which may be collected over water. The first portion of the gas often contains a little chlorine. The white saline residue in the flask is potassium chloride. This plan, which is very easy of execution, is always adopted when very pure gas is required for analytical purposes.

A third method, very good when perfect purity is not demanded, is to heat to redness, in an iron retort or gun-barrel, the black manganese oxide of commerce, which under these circumstances suffers decomposition, giving off part of its oxygen and leaving a lower oxide.

If a little of the black manganese oxide be finely powdered and mixed with potassium chlorate, and this mixture heated in a flask or retort by a lamp, oxygen will be disengaged with the utmost facility, and at a far lower temperature than when the chlorate alone is used. All the oxygen comes from the chlorate, the manganese remaining quite unaltered. The materials should be well dried in a capsule before their introduction into the flask. This experiment affords an instance of an effect by no means rare, in which a body seems to act by its mere presence, without taking any obvious part in the change brought about.

Methods for the preparation of oxygen on a large scale will be noticed under the heads of sulphuric acid and barium dioxide.

Oxygen is, bulk for bulk, a little heavier than atmospheric air, its specific gravity being 1·10563, referred to that of air as unity, and 15·96 referred to that of hydrogen as unity. A litre of oxygen at the standard temperature and pressure, that is to say, at 0° C., and 760 millimeters barometric pressure, weighs 1·43028 gram. At 15·5° C. (60° F.), and under a pressure of 30 inches, 100 cubic inches of the gas weigh 34·29 grains.

Combustion.—Oxygen is the sustaining principle of animal life, and of all the ordinary phenomena of combustion. Bodies which burn in the air burn with greatly increased splendour in oxygen gas. If a taper be blown out, and then introduced while the wick remains red-hot, it is instantly rekindled: a slip of wood or a match is relighted in the same manner. This effect is highly characteristic of oxygen, there being but one other gas which possesses the same property; and this is easily distinguished by other means. The experiment with the match is also constantly used as a rude test of the purity of the gas when it is about to be collected from the retort, or when it has stood for some time in contact with water exposed to air.

When a bit of charcoal is affixed to a wire, and plunged with a single point red-hot into a jar of oxygen, it burns with great brilliancy, throwing off beautiful scintillations, until, if the oxygen be in *excess*, it is completely consumed. An iron wire, or, still better, a

steel watch-spring, armed at its extremity with a bit of lighted amadou, and introduced into a vessel of oxygen gas, burns with great brilliancy. If the experiment be made in a jar standing on a plate, the fused globules of black iron oxide fix themselves in the glaze of the latter, after falling through a stratum of water half an inch in depth. Kindled sulphur burns with great beauty in oxygen; and phosphorus, under similar circumstances, exhibits a splendour which the eye is scarcely able to support. In each case the burning body enters into combination with the oxygen, forming a compound called an oxide.

When a compound burns in atmospheric air, the same ultimate effect is produced as in pure oxygen; the action is, however, less energetic, in consequence of the presence of nitrogen, which dilutes the oxygen and weakens its chemical powers. The process of respiration in animals is an effect of the same nature as ordinary combustion. The blood contains substances which slowly burn by the aid of the oxygen thus introduced into the system. When this action ceases, life becomes extinct.

It is necessary to bear in mind that combustion is not the same thing as ignition. When any solid substance capable of bearing the fire is heated to a certain point, it emits light, the character of which depends upon the temperature. Thus a bar of platinum or a piece of porcelain, raised to a particular temperature, becomes what is called red-hot, or emissive of red light: at a higher degree of heat, this light becomes whiter and more intense, and when urged to the utmost, as in the case of a piece of lime placed in the flame of the oxyhydrogen blowpipe, the light becomes exceedingly powerful, and acquires a tint of violet. Bodies in these states are said to be *incandescent* or *ignited*.

If now the same experiment be made on a piece of charcoal, similar effects will be observed; but something in addition; for whereas the platinum and porcelain, when removed from the fire, or the lime from the blow-pipe flame, immediately begin to cool, and emit less and less light, until they become quite dark, the charcoal maintains to a great extent its high temperature. Unlike the other bodies, too, which suffer no change whatever, either of weight or substance, the charcoal gradually wastes away until it disappears. This is what is called *combustion*, in contradistinction to mere ignition; the charcoal burns, and its temperature is kept up by the heat evolved in the act of union with the oxygen of the air.

In the most general sense, a body in a state of combustion is one in the act of undergoing intense chemical action: any chemical action whatsoever, if its energy rise sufficiently high, may produce the phenomenon of combustion, by *heating the body to such an extent that it becomes luminous*.

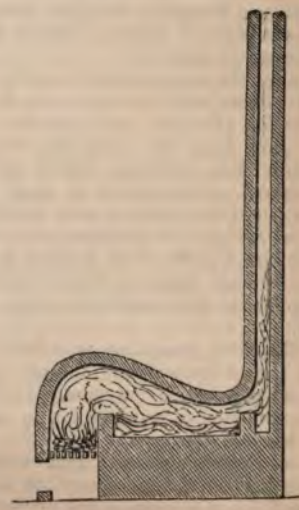
In all ordinary cases of combustion, the action lies between the burning body and the oxygen of the air; and since the materials employed for the economical production of heat and light consist

of carbon chiefly, or that substance conjoined with a certain proportion of hydrogen and oxygen, all common effects of this nature are cases of the rapid and violent oxidation of carbon and hydrogen by the aid of the free oxygen of the air. The heat is due to the act of chemical union, and the light to the elevated temperature.

By this principle, it is easy to understand the means which must be adopted to increase the heat of ordinary fires to the point necessary to melt refractory metals, and to bring about certain desired effects of chemical decomposition. If the rate of consumption of the fuel can be increased by a more rapid introduction of air into the burning mass, the intensity of the heat will of necessity rise in the same ratio, the quantity of heat evolved being fixed and definite for the same constant quantity of chemical action. This increased supply of air may be effected by two distinct methods: it may be forced into the fire by bellows or blowing-machines, as in the common forge and in the blast and cupola furnaces of the iron-worker; or it may be drawn through the burning materials by the help of a tall chimney, the fireplace being closed on all sides, and no entrance of air allowed, save between the bars of the grate. Such is the kind of furnace generally employed by the scientific chemist in assaying and in the reduction of metallic oxides by charcoal: the principle will be at once understood by the aid of the sectional drawing

Fig. 91.

Fig. 92.



(fig. 91), in which a crucible is represented arranged in the fire for an operation of the kind mentioned.

The "reverberatory" furnace (fig. 92) is one very much used in the arts when substances are to be exposed to heat without contact with the fuel. The fire-chamber is separated from the bed or hearth of the furnace by a low wall or *bridge* of brickwork, and the flame and heated air are reflected downwards by the arched form of the roof. Any degree of heat can be obtained in a furnace of this kind—from the temperature of dull redness to that required to melt very large quantities of cast-iron. The fire is urged by a chimney provided with a sliding-plate, or damper, to regulate the draught.

Solids and liquids, as melted metal, possess, when sufficiently heated, the faculty of emitting light; and the same power is exhibited by gaseous bodies, but the temperature required to render a gas luminous is incomparably higher than in the cases already described. Gas or vapour in this condition constitutes *flame*, the actual temperature of which generally exceeds that of the white heat of solid bodies.

The light emitted from pure flame is often very faint, but the illuminating power may be immensely increased by the presence of solid matter. The flame of hydrogen, or of a mixture of hydrogen and oxygen, is scarcely visible in full daylight; in a dusty atmosphere, however, it becomes much more luminous by igniting to intense whiteness the floating particles with which it comes in contact. A piece of lime in the blow-pipe flame (p. 153) cannot have a higher temperature than that of the flame itself, yet the light it throws off is infinitely greater.

It is possible, however, as pointed out by Dr. Frankland, to produce very bright flames in which no solid particles are present. Metallic arsenic burnt in a stream of oxygen produces an intense white flame, although both the metal itself and the product of its combustion (arsenious oxide) are gaseous at the temperature of the flame. The combustion of a mixture of nitrogen dioxide and carbon bisulphide also produces a dazzling white flame, without any separation of solid matter.

The conditions most essential to luminosity in a flame are a high temperature, and the presence of gases or vapours of considerable density. The effect of high temperature is seen in the greater brightness of the flame of sulphur, phosphorus, and indeed all substances, when burnt in pure oxygen, as compared with that which results from their combustion in common air; in the former case the whole of the substances present take part in the combustion, and generate heat, whereas in the latter the temperature is lowered by the presence of a large quantity of nitrogen, which contributes nothing to the effect. The relation between the luminosity of a flame and the vapour-densities of its constituents may be seen from the following table, in which the vapour-densities are referred to that of hydrogen as unity.

Relative Densities of Gases and Vapours.

Hydrogen	1	Arsenious chloride	90¾
Water	9	Phosphoric oxide	71, or 142
Hydrochloric acid	18¼	Metallic arsenic	150
Carbon dioxide	22	Arsenious oxide	198
Sulphur dioxide	32		

A comparison of these numbers shows that the brightest flames are those which contain the densest vapours. Hydrogen burning in chlorine produces a vapour more than twice as heavy as that resulting from its combustion in oxygen, and accordingly the light produced in the former case is stronger than in the latter; carbon and sulphur burning in oxygen produce vapours of still greater density, namely, carbon dioxide and sulphur dioxide, and their combustion gives a still brighter light; lastly, phosphorus, which has a very dense vapour, and likewise yields a product of great vapour-density, burns in oxygen with a brilliancy which the eye can scarcely endure. Moreover the luminosity of a flame is increased by condensing the surrounding gaseous atmosphere, and diminished by rarefying it. The flame of arsenic burning in oxygen may be rendered quite feeble by rarefying the oxygen; and, on the contrary, the faint flame of an ordinary spirit-lamp becomes very bright when placed under the receiver of a condensing-pump. Frankland has also found that candles give much less light when burning on the top of Mont Blanc than in the valley below, although the rate of combustion in the two cases is nearly the same. The effect of condensation in increasing the brightness of a flame is also strikingly seen in the combustion of a mixture of oxygen and hydrogen, which gives but a feeble light when burnt under the ordinary atmospheric pressure, as in the oxy-hydrogen blow-pipe, but a very bright flash when exploded in the Cavendish eudiometer (p. 165), in which the water-vapour produced by the combustion is prevented from expanding.

Flameless Combustion.—Mr. Fletcher, of Warrington, has lately shown that it is possible to obtain extremely high temperatures by the combustion of hydro-carbons without the production of any visible flame. On directing a gas flame upon a large mass of iron wire till the metal becomes red-hot, and then gradually turning on a blast of air till the flame totally disappeared, the temperature was observed to increase as the flame became smaller, until, on its disappearance, the iron fused and ran into drops, the whole mass of metal at the same time becoming intensely heated, and remaining so, although not a trace of flame could be detected in a perfectly dark room. Hence it appears that visible flame is not necessary for the production of high temperatures, but rather that its presence may be regarded as a proof of imperfect combustion.*

Lamps, Candles.—The Blow-pipe.—Flames burning in the air,

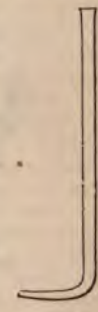
* Chemical News, vol. xlvi. pp. 22, 37.

and not supplied with oxygen from another source, are hollow, the chemical action being necessarily confined to the spot where the two bodies unite. That of a lamp or candle, when carefully examined, is seen to consist of three separate portions. The dark central part, easily rendered evident by depressing upon the flame a piece of fine wire-gauze, consists of combustible matter drawn up by the capillarity of the wick, and volatilised by the heat. This is surrounded by a highly luminous cone or envelope, which, in contact with a cold body, deposits soot. On the outside, a second cone may be traced, feeble in its light-giving power, but having an exceedingly high temperature. The most probable explanation of these appearances is as follows:—Carbon and hydrogen are very unequal in their attraction for oxygen, the latter greatly exceeding the former in this respect: consequently, when both are present, and the supply of oxygen is limited, the hydrogen takes up the greater portion of the oxygen, to the exclusion of a great part of the carbon. Now, this happens, in the case under consideration, at some little distance within the outer surface of the flame—namely, in the luminous portion, the little oxygen which has penetrated thus far inwards being mostly consumed by the hydrogen, and hydrocarbons being separated, rich in carbon and of great density in the state of vapour (naphthalene, chrysene, pyrene, &c.). These hydrocarbons, which would form smoke if they were cooler, and are deposited on a cold body held in the flame in the form of soot,* become intensely ignited by the burning hydrogen, and evolve a light whose whiteness marks a very elevated temperature. In the exterior and scarcely visible cone, these hydrocarbons undergo combustion.

Fig. 93.

A jet of coal-gas exhibits the same phenomena; but, if the gas be previously mingled with air, or if air be forcibly mixed with, or driven into, the flame, no such separation of carbon occurs; the hydrogen and carbon burn together, forming vapours of much lower density, and the illuminating power almost disappears.

Fig. 94.



The common mouth blow-pipe is an instrument of great utility. It is made of various shapes, the simplest and most generally used consisting of a brass tube bent as in fig. 94, and terminating in a narrow aperture.

The flame so produced is very peculiar. Instead of the double envelope just described, two long pointed cones are observed (fig. 95), which, when the blow-pipe is good, and the aperture smooth and

* Soot is not pure carbon, but a mixture of heavy hydrocarbons.

round, are very well defined, the outer cone being yellowish, and the inner blue. A double combustion is, in fact, going on, by the blast in the inside, and by the external air. The space between the inner and outer cones is filled with exceedingly hot combustible matter, possessing strong reducing or deoxidising powers, while the highly heated air just beyond the point of the exterior cone oxidises with great facility.

Fig. 95.

A small portion of matter, supported on a piece of charcoal, or fixed in a ring at the end of a fine platinum wire, can thus in an instant be exposed to a very high degree of heat under these contrasted circumstances, and observations of great value made in a very short time. The use of the instrument requires an even and uninterrupted blast of some duration, by a method easily acquired with a little patience: it consists in employing for the purpose the muscles of the cheeks alone, respiration being conducted through the nostrils, and the mouth from time to time replenished with air, without intermission of the blast.

The Argand lamp, adapted to burn either oil or spirit, but especially the latter, is a very useful piece of chemical apparatus. In this lamp the wick is cylindrical, the flame being supplied with air both inside and outside: the combustion is greatly aided by the chimney, which is made of copper when the lamp is used as a source of heat.

Fig. 96 exhibits, in section, an excellent lamp of this kind for burning alcohol or wood-spirit. It is constructed of thin copper, and furnished with ground caps to the wick-holder and aperture,*

Fig. 96.

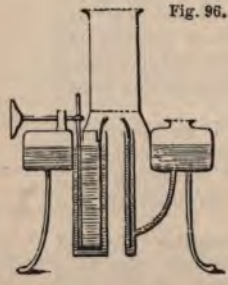


Fig. 97.

* When in use, this aperture must always be open, otherwise an accident is sure to happen; the heat expands the air in the lamp, and the spirit is forced out in a state of inflammation.

by which the spirit is introduced, in order to prevent loss when the lamp is not in use. Glass spirit-lamps (fig. 97), fitted with caps to prevent evaporation, are very convenient for occasional use, being always ready and in order.

In London, and other large towns where coal-gas is to be had, it is constantly used with the greatest economy and advantage in every respect as a source of heat. Retorts, flasks, capsules, and other vessels, can be thus exposed to an easily regulated and invariable temperature for many successive hours. Small platinum crucibles may be ignited to redness by placing them over the flame on a little wire triangle. The arrangement shown in fig. 98, consisting of a common Argand gas-burner fixed on a heavy and low foot, and connected with a flexible tube of caoutchouc or other material, is very convenient.

Fig. 98.

Fig. 99.

A higher temperature, and perfectly smokeless flame, is, however, obtained by burning the gas previously mixed with air. Such a flame is easily produced by placing a cap of wire-gauze on the chimney of the Argand burner just described, and setting fire to the gas above the wire-gauze. The flame does not penetrate below, but the gas, in passing up the chimney, becomes mixed with air, and this mixture burns above the cap with a blue, smokeless flame.

Another kind of burner for producing a smokeless flame has been contrived by Professor Bunsen, and is now used in all chemical laboratories. In this burner (fig. 99) the gas, supplied by a flexible tube *t*, passes through a set of small holes into the box at *a*, in which it mixes with atmospheric air, entering freely by a number of holes near the top of the box. The gaseous mixture passes up the tube *b*, and is inflamed at the top, where it burns with a tall, blue, smokeless flame, giving very little light, but much heat. By arranging two or more such tubes, together with an air-box containing a sufficient number of holes, a very powerful burner may be constructed.

Considerable improvements in this form of burner have been

made by Mr. Griffin, who has also constructed, on the same principle, powerful gas-furnaces, affording heat sufficient for the decomposition of silicates, and the fusion of considerable quantities of copper or iron.* Mr. Fletcher, of Warrington, has also introduced several new and very powerful forms of gas burners and furnaces, for use, not only in the laboratory, but also for manufacture and domestic purposes. The principle of burning a mixture of gas and air is also applied in Hofmann's gas-furnace for organic analysis, which will be described under Organic Chemistry.

The *kindling-point*, or temperature at which combustion commences, is very different with different substances; phosphorus will sometimes take fire in the hand; sulphur requires a temperature exceeding that of boiling water; charcoal must be heated to redness. Among gaseous bodies similar differences are observed; hydrogen is inflamed by a red-hot wire; light carburetted hydrogen requires a white heat to kindle it. When flame is cooled by any means below the temperature at which the rapid oxidation of the combustible gas occurs, it is at once extinguished. Upon this depends the principle of Sir H. Davy's invaluable *Safety-lamp*.

Light carburetted hydrogen, or marsh-gas, is frequently disengaged in large quantities in coal mines. This gas, mixed with seven or eight times its volume of atmospheric air, becomes highly explosive, taking fire at a light and burning with a pale-blue flame; and many fearful accidents have occurred from the ignition of large quantities of mixed gas and air occupying the extensive galleries and workings of a mine. Davy undertook an investigation with a view to discover some remedy for this constantly occurring calamity; and his labours resulted in some exceedingly important discoveries respecting flame, which led to the construction of the lamp which bears his name.

When two vessels filled with a gaseous explosive mixture are connected by a narrow tube, and the contents of one are fired by the electric spark, or otherwise, the flame is not communicated to the other, provided the diameter of the tube, its length, and the conducting power for heat of its material, bear a certain proportion to each other; the flame is extinguished by cooling, and its transmission rendered impossible.

In this experiment, high conducting power and diminished diameter compensate for diminution in length; and to such an extent can this be carried, that metallic gauze, which may be looked upon as a series of very short square tubes arranged side by side, when of sufficient degree of fineness, arrests in the most complete manner the passage of flame in explosive mixtures. Now the fire-damp mixture has an exceedingly high kindling point; a red heat does not cause inflammation; consequently, the gauze will be safe for this substance, when flame will pass in almost any other case.

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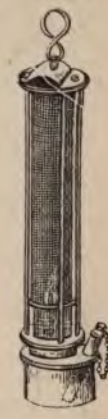
* See the article on Gas-burners and Furnaces in Watts's Dictionary *of Chemistry*, ii. 782.

The miner's safety lamp is merely an ordinary oil-lamp, the flame of which is enclosed in a cage of wire gauze, made double at the upper part, and containing about 400 apertures to the square inch. The tube for supplying oil to the reservoir reaches nearly to the bottom of the latter, while the wick admits of being trimmed by a bent wire passing with friction through a small tube in the body of the lamp; the flame can thus be kept burning for any length of time, without the necessity of unscrewing the cage. When this lamp is taken into an explosive atmosphere, although the fire-damp may burn within the cage with such energy as sometimes to heat the metallic tissue to dull redness, the flame is not communicated to the mixture on the outside.

Fig. 100.



These effects may be conveniently studied by suspending the lamp in a large glass jar, and gradually admitting coal-gas below. The oil-flame is at first elongated, and then, as the proportion of gas increases, extinguished, while the interior of the gauze cylinder becomes filled with the burning mixture of gas and air. As the atmosphere becomes pure, the wick is once more relighted. These appearances are so remarkable that the lamp becomes an admirable indicator of the state of the air in different parts of the mine.*

Oxy-hydrogen Flame.—It has already been stated that though the light emitted by hydrogen burning in the air or in oxygen gas is very feeble, nevertheless the temperature of the flame is very high. A still hotter flame may be produced by mixing the hydrogen with exactly the quantity of oxygen required for complete combination, that is, as will presently be seen, with half its own volume. Such a mixture burns like gunpowder, independently of the external air; and if a vessel or a bladder be filled with it, and a lighted match or a red-hot wire applied to the mouth, the two gases instantly unite throughout their entire mass, producing a loud report, and an explosive force sufficient to shatter any glass vessel of ordinary strength. On the other hand, by bringing a jet of oxygen within a hydrogen flame burning from a platinum nozzle, a

* This is the true use of the lamp, namely, to permit the viewer or superintendent, without risk to himself, to examine the state of the air in every part of the mine; not to enable workmen to continue their labours in an atmosphere habitually explosive, which must be unfit for human respiration, although the evil effects may be slow to appear. Owners of coal-mines should be compelled either to adopt efficient means of ventilation, or to close workings of this dangerous character altogether.

very hot flame may be produced without the slightest danger of explosion. This is effected by Daniell's oxy-hydrogen blow-pipe (fig. 101), in which the two gases are supplied from separate vessels, large gas-holders, for example, or air-tight bags of macintosh cloth pressed by weights, and suffered to mix only in the jet itself. The eye soon becomes accustomed to the peculiar appearance of the true oxy-hydrogen flame, so as to permit the supply of each gas to be exactly regulated by suitable stop-cocks attached to the jet. The flame thus produced is *solid*, the combustion taking place simultaneously throughout its mass, whereas all ordinary flames, as already observed (p. 157), whether burning in air or in pure oxygen, are hollow, the combustion in them taking place only at the surface.

Fig. 101.

A piece of thick platinum wire introduced into the flame of the oxy-hydrogen blow-pipe melts with the greatest ease; a watch-spring or a small steel file burns with the utmost brilliancy, throwing off showers of beautiful sparks; an incombustible oxidised body, as magnesia or lime, becomes so intensely ignited as to glow with a light insupportable to the eye, and to be susceptible of employment as a most powerful illuminator, as a substitute for the sun's rays in the solar microscope, and for night signals in trigonometrical surveys.

Slow Combustion.—Oxygen and hydrogen may be kept mixed at common temperatures for any length of time without combination taking place, but, under particular circumstances, they unite quietly and without explosion. Many years ago, Döbereiner made the curious observation, that finely divided platinum possesses the power of determining the union of the gases; and, subsequently, Faraday showed that the state of minute division is by no means indispensable, since rolled plates of the metal have the same property, provided their surfaces are absolutely clean. Neither is the effect strictly confined to platinum; other metals, as palladium and gold, and even stones and glass, exhibit the same property, although in a far lower degree, since they often require to be aided by a little heat. When a piece of platinum foil, which has been cleaned by hot oil of vitriol and thorough washing with distilled water, is thrust into a jar containing a mixture of oxygen and hydrogen standing over water, combination of the two gases immediately begins, and the level of the water rapidly rises, whilst the platinum becomes so hot that drops of water accidentally falling upon it enter into ebullition. If the metal be very thin and quite clean, and the gases pure, its temperature rises after a time to actual redness, and the residue of the mixture explodes. But this is an effect altogether *accidental*, and dependent upon the high temperature of the

platinum, which high temperature has been produced by the preceding quiet combination of the two bodies. When the platinum is reduced to a state of minute division, and its surface thereby much extended, it becomes immediately red-hot in a mixture of hydrogen and oxygen, or hydrogen and air ; a jet of hydrogen thrown upon a little of the spongy metal, contained in a glass or capsule, is at once kindled, and on this principle machines for the production of instantaneous light have been constructed. These, however, act well only when constantly used ; the spongy platinum is apt to become damp by absorption of moisture from the air, and its power is then for the time lost.

The best explanation that can be given of these curious effects is to suppose that solid bodies in general have, to a greater or less extent, the property of condensing gases upon their surfaces, or even liquefying them (as shown p. 139), and that this faculty is exhibited pre-eminently by certain of the non-oxidisable metals, as platinum and gold. Oxygen and hydrogen may thus, under these circumstances, be brought, as it were, within the sphere of their mutual attractions by a temporary increase of density, whereupon combination ensues.

Coal-gas and ether or alcohol vapour may also be made to exhibit the phenomenon of quiet oxidation under the influence of this remarkable surface-action. A close spiral of slender platinum wire, a roll of thin foil, or even a common platinum crucible, heated to dull redness, and then held in a jet of coal-gas, becomes strongly ignited, and remains in that state as long as the supply of mixed gas and air is kept up, the temperature being maintained by the heat disengaged in the act of union. Sometimes the metal becomes white-hot, and then the gas takes fire.

If such a coil of wire be attached to a card, and suspended in a glass containing a few drops of ether, having previously been made red-hot in the flame of a spirit-lamp, it will continue to glow until the oxygen of the air is exhausted, giving rise to the production of an irritating vapour which attacks the eyes. The combustion of the ether is in this case but partial ; a portion of its hydrogen is alone removed, and the whole of the carbon left untouched.

Fig. 102.

A coil of thin platinum wire may be placed over the wick of a spirit-lamp, or a ball of spongy platinum sustained just above the cotton ; on lighting the lamp, and then blowing it out as soon as the metal appears red-hot, slow combustion of the spirit drawn up by the capillarity of the wick will take place, accompanied by the pungent vapours just mentioned, which may be modified, and even rendered agreeable, by dissolving in the liquid some sweet-smelling essential oil or resin.

Oxides of Hydrogen.—There are two oxides of hydrogen—namely, the monoxide, which is water, and the dioxide, discovered in the year 1818 by Thénard.

It appears that the composition of water was first demonstrated in the year 1781 by Cavendish;* but the discovery of the exact proportions in which oxygen and hydrogen unite in generating that most important compound has, from time to time to the present day, occupied the attention of some of the most distinguished cultivators of chemical science. There are two distinct methods of research in chemistry—the *analytical*, or that in which the compound is resolved into its elements, and the *synthetical*, in which the elements are made to unite and produce the compound. The first method is of much more general application than the second; but in this particular instance both may be employed, although the results of the synthesis are the more valuable.

The decomposition of water may be effected by voltaic electricity. When water is acidulated so as to render it a conductor,† and a portion interposed between a pair of platinum plates connected with the extremities of a voltaic apparatus of moderate power, decomposition of the liquid takes place in a very interesting manner; oxygen, in a state of perfect purity, is evolved from the water in contact with the plate belonging to the copper end of the battery, and hydrogen, equally pure, is disengaged at the plate connected with the zinc extremity, the middle portions of liquid remaining apparently unaltered. By placing small graduated jars over the platinum plates, the gases can be collected, and their quantities determined. The whole arrangement is shown in fig. 103; the conducting wires pass through the bottom of the glass cup, and away to the battery.

Fig. 103.

When this experiment has been continued for a sufficient time, it will be found that the volume of the hydrogen is a *very* little above twice that of the oxygen. Were it not for the accidental circumstance of oxygen being sensibly more soluble in water than hydrogen, the proportion of two to one by measure would come out exactly.

Water, as Sir W. Grove has shown, is likewise decomposed into its constituents by heat. This effect is produced by introducing

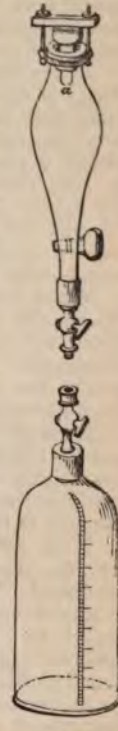
* A claim to the discovery of the composition of water, on behalf of James Watt, has been very strongly urged, and supported by such evidence that the reader of the controversy may be led to the conclusion that the discovery was made by both parties, nearly simultaneously, and unknown to each other. See the article "Gas," by Dr. Paul, in Watts's Dictionary of Chemistry, ii. 780.

† See the section on "Electro-Chemical Decomposition."

platinum balls, intensely ignited by electricity or other means, into water or steam. The two gases are obtained in very small quantities at a time.

When oxygen and hydrogen, both as pure as possible, are mixed in the proportions mentioned, passed into a strong glass tube standing over mercury, and exploded by the electric spark, all the mixture disappears, and the mercury is forced up into the tube, filling it completely. The same experiment may be made with the explosion vessel or eudiometer of Cavendish (fig. 104). The instrument is exhausted at the air-pump, and then filled from a capped jar with the mixed gases; on passing an electric spark by the wires shown at *a*, explosion ensues, and the glass becomes bedewed with moisture; and if the stop-cock be then opened under water, the latter will rush in and fill the vessel, leaving merely a bubble of air, the result of imperfect exhaustion.

Fig. 104.



But the process upon which most reliance is placed for demonstrating the composition of water, is that in which pure copper oxide is reduced at a red heat by hydrogen, and the water so formed is collected and weighed. This oxide suffers no change by heat alone, but the momentary contact of hydrogen, or any common combustible matter, at a high temperature, suffices to reduce a corresponding portion to the metallic state. Fig. 105 will serve to convey some idea of the arrangement adopted in researches of this kind.

A copious supply of hydrogen is procured by the action of dilute sulphuric acid upon the purest zinc that can be obtained; and the gas is made to pass in succession through solutions of silver nitrate and strong caustic potash, by which its purification is completed. After this it is conducted through a tube three or four inches long, filled with fragments of pumice-stone steeped in concentrated oil of vitriol, or with phosphoric anhydride. These substances have so great an attraction for aqueous vapour, that they dry the gas completely

Fig. 105.

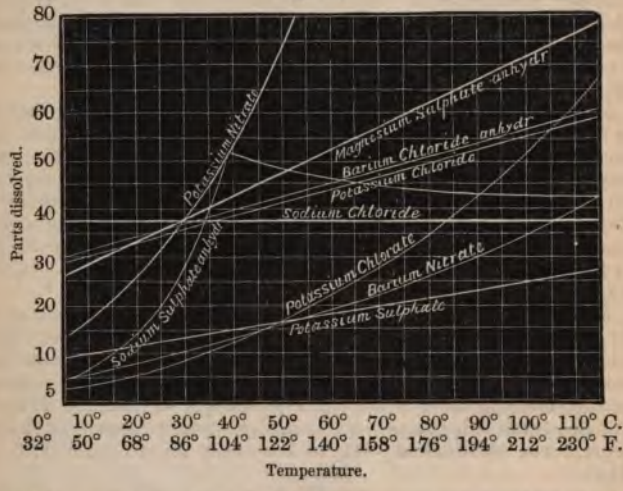
during its transit. The extremity of this tube is shown at *a*. The dry hydrogen thus arrives at the part of the apparatus containing

certain organic salts of calcium dissolve more freely in cold than in hot water.

Fig. 106 exhibits the unequal solubility of different salts in water of different temperatures. The *lines of solubility* cut the verticals

Solubility of Salts in 100 *parts of Water.*

Fig. 106.



raised from points indicating the temperatures upon the lower horizontal line, at heights proportioned to the quantities of salt dissolved by 100 parts of water. The diagram shows, for example, that 100 parts of water dissolve, of potassium sulphate 8 parts at 0° C., 17 parts at 50°, and 25 parts at 100°. There are salts which, like sodium chloride, possess, as already mentioned, very nearly the same degree of solubility in water at all temperatures; in others, like potassium sulphate or potassium chloride, the solubility increases directly with the increment of temperature; in others, again, like potassium nitrate or potassium chlorate, the solubility augments much more rapidly than the temperature. The differences in the deportment of these different salts are shown very conspicuously, by a straight horizontal line, by a straight inclined line, and lastly by curves, the convexity of which is turned towards the lower horizontal line.

The solubility of a salt is usually represented by the quantity of anhydrous salt dissolved by 100 parts of water. It is obvious, however, that salts containing water of hydration or water of crystallisation cannot, within certain limits of temperature, dissolve in

water in the anhydrous state, but must be dissolved as hydrates. The solubility of a hydrated salt frequently differs very considerably from that of the same salt in the anhydrous state. Again, many salts, as already observed, form more than one hydrate; and these several hydrates may also differ in their solubility. Sodium sulphate forms a hydrate, $SO_4Na_2 + 7H_2O$, consisting, in 100 parts, of 53 parts of anhydrous salt and 47 parts of water, which is obtained in crystals when a solution of sodium sulphate saturated at 100° C. is cooled out of contact with the air: this hydrate is much more soluble than the ordinary hydrate, $SO_4Na_2 + 10H_2O$ (Glauber's salt), which differs from the former in its crystalline form, and consists, in 100 parts, of 44·2 parts of anhydrous salt and 55·8 parts of water. When a solution of sodium sulphate is saturated at the boiling point of water, and cooled to the common temperature without depositing any crystals, the salt exists in the form of the more soluble hydrate. This salt, when coming in contact with the dust of the air, or with a small crystal of common Glauber's salt, is suddenly transformed into the less soluble hydrate, part of which separates from the solution in the form of Glauber's salt. From 0° to 33° C. (32° to 91° F.) sodium sulphate dissolves as Glauber's salt, the solubility of which increases with the temperature: hence the rapid rise of the curve representing the solubility of the salt. Above 33° C. the hydrate of sodium sulphate is decomposed, even in solution, being more and more thoroughly converted into the anhydrous salt as the temperature increases. Sodium sulphate appears, however, far less soluble in the anhydrous state, and hence the diminution of solubility of the salt when its solution is heated above 33° C.

Liquid Diffusion. Dialysis.—When a solution having a density greater than that of water is introduced into a cylindrical glass vessel, and then water very cautiously poured upon it, in such a manner that the two layers of liquid remain unmoved, the substance dissolved in the lower liquid will gradually pass into the supernatant water, though the vessel may have been left undisturbed, and the temperature remain unchanged. This gradual passage of a dissolved substance from its original solution into pure water, taking place notwithstanding the higher specific gravity of the substance which opposes this passage, is called the *diffusion of liquids*. The phenomena of this diffusion were elaborately investigated by Graham, who arrived at very important results. Different substances, when in solution of the same concentration, and under other similar circumstances, diffuse with very unequal velocity. Hydrochloric acid, for instance, diffuses with greater rapidity than potassium chloride, potassium chloride more rapidly than sodium chloride, and the latter, again, more quickly than magnesium sulphate; gelatin, albumin, and caramel diffuse very slowly. Diffusion is generally found to take place more rapidly at high than at low temperatures. It is more particularly rapid with crystallised sub-

stances, though not exclusively, for hydrochloric acid and alcohol are among the highly diffusive bodies; slow with non-crystalline bodies, which, like gelatin, are capable of forming a jelly, though even here exceptions are met with. Graham calls the substances of great diffusibility *crystalloïds*, the substances of low diffusibility *colloïds*. The unequal power of diffusion with which different substances are endowed frequently furnishes the means of separating them. When water is poured with caution, so as to prevent mixing, upon a solution containing equal quantities of potassium chloride and sodium chloride, the more diffusible potassium chloride travels more rapidly upwards than the less diffusible sodium chloride, and very considerable portions of potassium chloride will have reached the upper layers of the water before the sodium chloride has arrived there in appreciable quantity. The separation of rapidly diffusible crystalloïds and slowly diffusible colloïds succeeds still better.

A more complete separation of crystalloïds and colloïds may be accomplished in the following manner:—Graham made the important observation, that certain membranes, and also parchment paper, when in contact, on the one surface, with a solution containing a mixture of crystalloïdal and colloïdal substances, and, on the other surface, with pure water, will permit the passage to the water of the crystalloïds, but not of the colloïds. To carry out this important mode of separation, which is designated by the term *dialysis*, the lower mouth of a glass vessel, open on both sides (fig. 107), is tied over with parchment paper placed upon an appropriate support (fig. 108), and transferred, together with the latter, into a

Fig. 107.

Fig. 108.

Fig. 109.

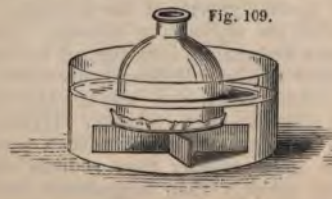


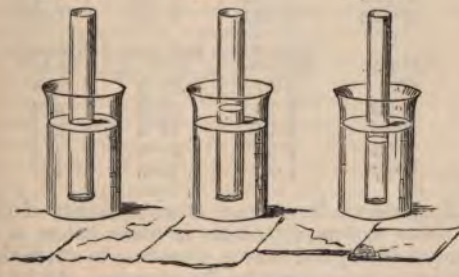
Fig. 110.

larger vessel filled with water (fig. 109); or the vessel may be suspended, as shown in fig. 110. The liquid containing the different

substances in solution is then poured into the inner vessel, so as to form a layer of about half an inch in height upon the parchment paper. The crystalloïdal substances gradually pass through the parchment paper into the outer water, which may be renewed from time to time; the colloïdal substances are almost entirely retained by the liquid in the inner vessel. In this manner Graham prepared several colloïds free from crystalloïds; he showed, moreover, that poisonous crystalloïds, such as arsenious acid or strychnine, even when mixed with very large proportions of colloïdal substances, pass over into the water of the dialyser in such a state of purity that their presence may be established by re-agents with the utmost facility.

Osmose.—When two different liquids are separated by a porous diaphragm, as, for instance, by a membrane, and the liquids mix through this diaphragm, it is found that in most cases the quantities travelling in opposite directions are unequal. Suppose three cylinders, the lower mouths of which are tied over with bladders, to be filled respectively with concentrated solutions of copper sulphate, sodium chloride, and alcohol, and let them be immersed in vessels containing water, to such a depth that the liquids inside and outside are level (fig. 111). After some time the liquid within the tube is found to have risen appreciably above the level of the water (fig. 112). On the other hand, if the cylinder filled with pure water be immersed in a solution of copper sulphate, or of sodium chloride, or in alcohol, the liquid in the cylinder is seen to diminish after some time (fig. 113). A quantity of water passes through the

Fig. 111. Fig. 112. Fig. 113.



bladder into the solution of copper sulphate or sodium chloride, or into alcohol, larger than the amount of either of these three liquids which passes through the bladder into the water. The mixing of dissimilar substances through a porous diaphragm is called *osmose.* The passage in larger proportions of one liquid into another is designated by the term *exosmose.*

These phenomena are due to the attraction which the two liquids

have for each other, and to the difference of the attraction exercised by the diaphragm upon these liquids. Bladder takes up a much larger quantity of water than of a solution of salt or of alcohol. Very rarely only one of the liquids traverses the diaphragm; generally two currents of unequal strength move in opposite directions. When water is separated by an animal membrane from a solution of salt or from alcohol, not only is a transition of water to these liquids observed, but a small quantity of hydrochloric acid and of alcohol also passes over into the water. In some cases, however, when colloïdal substances in concentrated solutions are on one side of the diaphragm and water on the other, the latter alone traverses the diaphragm, not a trace of the former passing through to the water.

Water likewise dissolves gases. Solution of gases in water (or in other liquids) is called *absorption*, unless this solution gives rise to the formation of chemical compounds in definite proportions. The phenomena of absorption have been more particularly studied by Bunsen, to whom we are indebted for the most accurate examination of this subject.

Water dissolves very unequal quantities of the different gases, and very unequal quantities of the same gas at different temperatures. 1 vol. of water absorbs, at the temperatures stated in the table, and under the pressure of 30 inches of mercury, the following volumes of different gases, measured at 0° C. and 30 inches pressure:—

	Oxygen.	Nitrogen.	Hydrogen.	Nitrogen Monoxide.	Carbon Dioxide.
0° C.	0·041	0·020	0·019	1·31	1·80
10°	0·033	0·016	0·019	0·92	1·18
20°	0·028	0·014	0·019	0·67	0·90

	Chlorine.	Hydrogen Sulphide.	Sulphurous Oxide.	Hydrochloric Acid.	Ammonia.
0° C.	—	4·37	53·9	505	1180
10°	2·59	3·59	36·4	472	898
20°	2·16	2·91	27·3	441	680
30°	1·75	2·33	20·4	412	536
40°	1·37	1·86	15·6	387	444

When the pressure increases, a larger quantity of the gases is absorbed. Gases moderately soluble in water follow in their solubility the law of Henry and Dalton, according to which the quantity of gas dissolved is proportional to the pressure. At 10° C. 1 vol. of water absorbs, under a pressure of 1 atmosphere, 1·18 vol. of carbon dioxide, measured at 0° and under a pressure of 30 inches mercury. The quantity of carbon dioxide dissolved under a pressure of 2 atmospheres, and measured under conditions precisely similar to those of the previous experiments, equals 2·36 vols. Again, 1 vol. of water dissolves, under a pressure of ½ atmosphere, 0·59 vol. of carbon dioxide also measured at 0° and under 30 inches of mercury. Gases which are exceedingly soluble in water do not obey this law,

except at higher temperatures, when the solubility has been already considerably diminished.

It deserves, however, to be noticed, that the pressure which determines the rate of absorption of a gas is by no means the general pressure to which the absorbing liquid is exposed, but that pressure which the gas under consideration would exert if it were alone present in the space with which the absorbing liquid is in contact. Thus, supposing water to be in contact with a mixture of 1 vol. of carbon dioxide and 3 vols. of nitrogen, under a pressure of 4 atmospheres, the amount of carbon dioxide dissolved by the water will be by no means equal to that which the water would have absorbed if it had been, at the same pressure of 4 atmospheres, in contact with pure carbon dioxide. In a mixture of carbon dioxide and nitrogen in the stated proportions, the carbon dioxide exercises only $\frac{1}{4}$, the nitrogen only $\frac{3}{4}$, of the total pressure of the gaseous mixture (4 atmospheres); the partial pressure due to the carbon dioxide is in this case 1 atmosphere, that due to the nitrogen 3 atmospheres; and water, though exposed to a pressure of 4 atmospheres, cannot, under these circumstances, absorb more carbon dioxide than it would if it were in contact with pure carbon dioxide under a pressure of 1 atmosphere.

It is necessary to bear this in mind in order to understand why the air which is absorbed by water out of the atmosphere differs in composition from atmospheric air. The latter consists very nearly of 21 vols. of oxygen and 79 vols. of nitrogen. In atmospheric air which acts under a pressure of 1 atmosphere, the oxygen exerts a partial pressure of $\frac{21}{100}$, the nitrogen a partial pressure of $\frac{79}{100}$ atmosphere. At 10° C. 1 vol. of water (see the above table) absorbs 0·033 vol. of oxygen and 0·016 vol. of nitrogen, supposing these gases to act in the pure state under a pressure of 1 atmosphere. But under the partial pressures just indicated, water of 10° C. cannot absorb more than $\frac{21}{100} \times 0{\cdot}033 = 0{\cdot}007$ of oxygen, and $\frac{79}{100} \times 0{\cdot}016 = 0{\cdot}13$ vol. of nitrogen. In $0{\cdot}007 + 0{\cdot}013 = 0{\cdot}020$ vol. of the gaseous mixture absorbed by water there are consequently 0·007 vol. of oxygen, and 0·013 vol. of nitrogen, or in 20 vols. of this mixture, 7 vols. of oxygen, and 13 vols. of nitrogen, or in 100 vols. of the gaseous mixture, 35 vols. of oxygen and 65 vols. of nitrogen. The air contained at the common temperature in water is thus seen to be very much richer in oxygen than ordinary atmospheric air.

This property of water to absorb oxygen from the air more readily than nitrogen has been applied to the preparation of oxygen for industrial use.* Air is pressed into water by means of a forcing-pump, and the gases which escape on diminishing the pressure are subjected to the same treatment eight times in succession, by which time nearly pure oxygen is obtained. The following table shows the composition of the gaseous mixture at each successive stage:—

* Mallet, Dingler's Polyt. Journal, cxciv. 112.

Atmospheric Air.	Composition after successive Pressures.							
	1	2	3	4	5	6	7	8
N . . 79	66·67	52·5	37·5	25·0	15·0	9·0	5·0	2·7
O . . 21	33·33	47·5	62·5	75·0	85·0	91·0	95·0	97·3

Water containing a gas in solution, when exposed in a vacuum or in a space filled with another gas, allows the gas absorbed to escape until the quantity retained corresponds with the share of the pressure belonging to the gas evolved. If the latter be constantly removed by a powerful absorbent or by a good air-pump, it is in most cases easy to separate every trace of gas from the water. The same result is obtained when water containing a gas in solution is exposed in a space of comparatively infinite size filled with another gas. Water in which nitrogen monoxide is dissolved loses the latter entirely by mere exposure to the atmosphere, and the gas evolved cannot, at any moment, exert more than an infinitely small share of the pressure. If water be freed from gases by ebullition, the separation depends partly upon the diminution of the solubility by the increase of temperature, partly also upon the formation above the surface of the liquid of a constantly renewed atmosphere into which the gas still retained by the liquid may escape.

Some gases which are absorbed in large quantities and very quickly by water—hydrochloric acid, for instance—cannot be perfectly expelled either by the protracted action of another gas (exposure to the atmosphere) or by ebullition; in such cases the liquid, still charged with gas, evaporates as a whole when it has assumed a certain composition. This composition varies, however, with the temperature if the liquid be submitted to a current of air, and with the pressure if it be boiled.

Liquids also lose the gas they contain in solution by freezing: hence the air-bubbles in ice, which consist of the air which had been absorbed from the atmosphere by the water. Gas is retained by liquids at the freezing temperature only when it forms a chemical combination in definite proportion with the liquid. Water containing chlorine or sulphurous acid in solution freezes without evolution of gas, with formation of a solid hydrate of chlorine or sulphurous acid.

Pure water generally dissolves gases more copiously than water containing solid bodies in solution (salt water, for instance). If in some few cases exceptions are observed to take place, they appear to depend upon the formation of feeble but true chemical compounds in definite proportion; the fact that carbon dioxide is more copiously absorbed by water containing sodium phosphate in solution than by pure water, may perhaps be explained in this manner.

When water is heated in a strong vessel to a temperature above

that of the ordinary boiling point, its solvent powers are still further increased. Dr. Turner enclosed in the upper part of a high-pressure steam-boiler, worked at 149° C. (300° F.), pieces of plate and crown glass. At the expiration of four months the glass was found completely corroded by the action of the water; what remained was a white mass of silica, destitute of alkali, while stalactites of siliceous matter, above an inch in length, depended from the little wire cage which enclosed the glass. This experiment tends to illustrate the changes which may be produced by the action of water at a high temperature in the interior of the earth upon felspathic and other rocks. The phenomenon is manifest in the Geyser springs of Iceland, which deposit siliceous sinter.

Hydrogen Dioxide, H_2O_2.—To prepare this compound, barium dioxide (obtained by igniting pure baryta in a stream of oxygen), is decomposed by dilute sulphuric acid (1 part of the strong acid to at least 5 parts of water), the reaction being represented by the equation :

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

The resulting solution of hydrogen dioxide is concentrated by evaporation in a vacuum over sulphuric acid (p. 66); if it begins to give off oxygen during the evaporation, the decomposition may be checked by adding a drop or two of sulphuric acid. It may thus be concentrated until it acquires the specific gravity of 1·45. In this state it is a colourless, transparent, inodorous liquid, very prone to decomposition, the least rise of temperature causing effervescence, due to the escape of oxygen gas; near 100° it is decomposed with explosive violence. The dilute aqueous solution (*oxygenated water*) is however much more stable, and is prepared as an article of commerce. It possesses powerful oxidising and bleaching properties, and is used as a disinfectant, and for cleansing old engravings and oil-paintings.

Hydrogen dioxide exhibits a remarkable reaction with certain easily reducible metallic oxides, the metal being reduced, and free oxygen evolved ; *e.g.*, with silver oxide :

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2.$$

This reaction will be further discussed hereafter.

Oxides and Oxy-acids of Chlorine.

There are four oxyacids of chlorine, which may be regarded as oxides of hydrochloric acid; thus—

	Formula.	Composition by weight. Hydrogen.		Chlorine.		Oxygen.
Hydrochloric acid .	HCl	1	+	35·4		
Hypochlorous acid .	$HClO$	1	+	35·4	+	16
Chlorous acid . .	$HClO_2$	1	+	35·4	+	32
Chloric acid . .	$HClO_3$	1	+	35·4	+	48
Perchloric acid .	$HClO_4$	1	+	35·4	+	64

The anhydrous chlorine oxides corresponding with hypochlorous and chlorous acids are also known, namely—

	Chlorine.		Chlorine.		Oxygen.
Chlorine monoxide, or Hypochlorous oxide, Cl_2O . .	35·4	+	35·4	+	16
Chlorine trioxide, or Chlorous oxide, Cl_2O_3 . . .	35·4	+	35·5	+	48

Also an oxide to which there is no corresponding acid, namely—

	Chlorine.		Oxygen.
Chlorine tetroxide, Cl_2O_4 . .	2 × 35·4	+	64

The oxides corresponding with chloric and perchloric acid have not been obtained.

Hypochlorous and chloric acids are produced by the action of chlorine on certain metallic oxides in presence of water; hypochlorous and chlorous acids also by direct oxidation of hydrochloric acid. Perchloric acid and chlorine tetroxide result from the decomposition of chloric acid.

Hypochlorous Oxide, Acid, and **Salts.**—The oxide is best prepared by the action of chlorine gas upon dry mercuric oxide. This oxide, prepared by precipitation, and dried by exposure to a strong heat, is introduced into a glass tube kept cool, and well-washed dry chlorine gas is slowly passed over it. Mercuric chloride ($HgCl_2$) and hypochlorous oxide are thereby formed; the latter is collected by displacement. The reaction by which it is produced is represented by the equation,

$$HgO + Cl_4 = Cl_2O + HgCl_2.$$

The mercuric chloride, however, does not remain as such; it combines with another portion of the oxide when the latter is in excess, forming a peculiar brown compound, an oxychloride of mercury, $HgCl_2,HgO$. It is remarkable that the *crystalline* mercuric oxide prepared by calcining the nitrate, or by the direct oxidation of the metal, is scarcely acted upon by chlorine under the circumstances described.

Hypochlorous oxide is a pale-yellow gaseous body, containing, in every two measures, two measures of chlorine and one of oxygen, and is therefore analogous in constitution to water. It explodes, although with no great violence, by slight elevation of temperature. Its odour is peculiar, and quite different from that of chlorine. When the flask or bottle in which the gas is received is exposed to artificial cold by the aid of a mixture of ice and salt, the hypochlorous oxide condenses to a deep-red liquid, slowly soluble in water, and very subject to explosion.

Hypochlorous acid is produced by the solution of hypochlorous oxide in water; also by passing air saturated with hydrochloric acid gas through a solution of potassium permanganate acidulated with hydrochloric acid and heated in a water-bath: the distillate is a

solution of hypochlorous acid, formed by oxidation of the hydrochloric acid; thirdly, by decomposing a metallic hypochlorite with sulphuric acid or other oxy-acid; fourthly, by passing chlorine gas into water holding in suspension a solution containing metallic oxides, hydroxides, carbonates, sulphates, phosphates, &c., the most advantageous for the purpose being mercuric oxide, or calcium carbonate (chalk), $CaCO_3$, the products in this case being carbon dioxide, calcium chloride, and hypochlorous acid:

$$CaCO_3 + H_2O + Cl_4 = CO_2 + CaCl_2 + 2HClO.$$

The aqueous solution of hypochlorous acid has a yellowish colour, an acid taste, and a characteristic sweetish smell. The strong acid decomposes rapidly even when kept in ice. The dilute acid is more stable, but is decomposed by long boiling into chloric acid, water, chlorine, and oxygen. Hydrochloric acid decomposes it, with formation of chlorine:

$$HClO + HCl = H_2O + Cl_2.$$

It is a very powerful bleaching and oxidising agent, converting many of the elements—iodine, selenium, and arsenic, for example—into their highest oxides, and at the same time liberating chlorine.

Metallic hypochlorites may be obtained in the pure state by neutralising hypochlorous acid with metallic hydroxides, such as those of sodium, calcium, copper, &c.; but they are usually prepared by passing chlorine gas into solutions of alkalis or alkaline carbonates, or over the dry hydroxides of the earth-metals. In this process a metallic chloride is formed at the same time. With dry slaked lime, for example, which is a hydroxide of calcium, CaH_2O_2, the products are calcium hypochlorite, $CaCl_2O_2$, calcium chloride, and water:

$$2CaH_2O_2 + Cl_4 = CaCl_2O_2 + CaCl_2 + 2H_2O.$$

The salts thus obtained constitute the bleaching and disinfecting salts of commerce. They will be more fully described under the head of Calcium Salts.

Chlorous Oxide, Acid, and Salts.—The oxide is prepared by heating in a flask filled to the neck, a mixture of four parts of potassium chlorate and three parts of arsenious oxide with 12 parts of nitric acid previously diluted with four parts of water. During the operation, which must be performed in a water-bath, a greenish-yellow gas is evolved, which is permanent in a freezing mixture of ice and salt, but liquefiable by extreme cold. It dissolves freely in water and in alkaline solutions, forming chlorous acid and metallic chlorites. The reaction by which chlorous oxide is formed is somewhat complicated. The arsenious oxide deprives the nitric acid of part of its oxygen, reducing it to nitrous acid, which is then reoxidised at the expense of the chloric acid, reducing it to chlorous oxide:

$$2HClO_3 + 2HNO_2 = 2HNO_3 + H_2O + Cl_2O_3.$$
Chloric acid. Nitrous acid. Nitric acid. Chlorous oxide.

Chlorous Acid may be prepared by condensing chlorous oxide in water, or by decomposing a metallic chlorite with dilute sulphuric or phosphoric acid. Its concentrated solution is a greenish-yellow liquid having strong bleaching and oxidising properties. It does not decompose carbonates, but acts strongly with caustic alkalis and earths to form chlorites.

Chlorine Tetroxide, Cl_2O_4.—When potassium chlorate is made into a paste with concentrated sulphuric acid, and cooled, and this paste is very cautiously heated by warm water in a small glass retort, a deep yellow gas is evolved, which is the body in question; it can be collected only by displacement, since mercury decomposes and water absorbs it.

Chlorine tetroxide has a powerful odour, quite different from that of the preceding compounds, and of chlorine itself. It is exceedingly explosive, being resolved with violence into its elements by a temperature short of the boiling point of water. Its preparation is, therefore, always attended with danger, and should be performed only on a small scale. It is composed by measure of one volume of chlorine and two volumes of oxygen, condensed into two volumes. It may be liquefied by cold. The solution of the gas in water bleaches.

The *euchlorine* of Davy, prepared by gently heating potassium chlorate with dilute hydrochloric acid, is probably a mixture of chlorine tetroxide and free chlorine.

The production of chlorine tetroxide from potassium chlorate and sulphuric acid depends upon the spontaneous splitting of the chloric acid into chlorine tetroxide and perchloric acid, which latter remains as a potassium salt.

$$6KClO_3 + 3H_2SO_4 = 2Cl_2O_4 + 2HClO_4 + 3K_2SO_4 + 2H_2O.$$
Potassium chlorate. Hydrogen sulphate. Hydrogen perchlorate. Potassium sulphate.

When a mixture of potassium chlorate and sugar is touched with a drop of oil of vitriol, it is instantly set on fire, the chlorine tetroxide disengaged being decomposed by the combustible substance with such violence as to cause inflammation. If crystals of potassium chlorate be thrown into a glass of water, a few small fragments of phosphorus added, and then oil of vitriol poured down a narrow funnel reaching to the bottom of the glass, the phosphorus will burn beneath the surface of the water, by the assistance of the oxygen of the chlorine tetroxide disengaged. The liquid at the same time becomes yellow, and acquires the odour of that gas.

Chloric Acid, $HClO_3$.—This is the most important compound of the series. When chlorine is passed to saturation into a moderately

strong hot solution of potassium hydroxide or carbonate, and the liquid concentrated by evaporation, it yields, on cooling, flat tabular crystals of a colourless salt, consisting of potassium chlorate. The mother-liquor contains potassium chloride:

$$\underset{\text{Potassium oxide.}}{3K_2O} + Cl_6 = \underset{\text{Potassium chloride.}}{5KCl} + \underset{\text{Potassium chlorate.}}{KClO_3}.$$

From potassium chlorate, chloric acid may be obtained by boiling the salt with a solution of hydrofluosilicic acid, which forms an almost insoluble potassium salt, decanting the clear liquid, and digesting it with a little silica, which removes the excess of the hydrofluosilicic acid. Filtration through paper must be avoided.

By cautious evaporation, the acid may be so far concentrated as to assume a syrupy consistence; it is then very easily decomposed. It sometimes sets fire to paper, or other dry organic matter, in consequence of the facility with which it is deoxidised by combustible bodies.

The chlorates are easily recognised; they give no precipitate when in solution with silver nitrate; they evolve pure oxygen when heated, passing thereby into chlorides; and they afford, when treated with sulphuric acid, the characteristic explosive yellow gas already described. The dilute solution of the acid has no bleaching power.

Perchloric Acid, $HClO_4$.—When powdered potassium chlorate is thrown by small portions at a time into hot nitric acid, a change takes place of the same description as that which happens when sulphuric acid is used, but with this important difference, that the chlorine and oxygen, instead of being evolved in a dangerous state of combination, are emitted in a state of *mixture*. The result of the action is a mixture of potassium nitrate and perchlorate, which may be readily separated by their difference of solubility.

Perchloric acid is obtained by distilling potassium perchlorate with sulphuric acid. Pure perchloric acid is a colourless liquid, of sp. gr. 1·782 at 15·5°, not solidifying at − 35°; it soon becomes coloured, even if kept in the dark, and after a few weeks decomposes with explosion. The vapour of perchloric acid is transparent and colourless: in contact with moist air it produces dense white fumes. The acid, when cautiously mixed with a small quantity of water, solidifies to a crystalline mass, which is a compound of perchloric acid with one molecule of water, $HClO_4 + H_2O$. When brought in contact with carbon, ether, or other organic substances, perchloric acid explodes with nearly as much violence as chloride of nitrogen.

Oxy-acids of Bromine.

Hypobromous Acid, HBrO, is formed by agitating bromine-water with mercuric oxide, according to the equation:

$$HgO + 2Br_2 + H_2O = HgBr_2 + 2HOBr.$$

The greater part of the hypobromous acid contained in the resulting solution is resolved on distillation into bromine and oxygen, but the acid may be distilled in a vacuum at 40°, without decomposition. Aqueous hypobromous acid is a light straw-yellow liquid, which resembles hypochlorous acid in its properties, is a powerful oxidising agent, and bleaches vegetable colours.

Bromic Acid, $HBrO_3$.—Caustic alkalis react with bromine, in the same manner as with chlorine, yielding a bromide and bromate, which may be separated by the inferior solubility of the latter. Bromic acid, obtained from barium bromate, closely resembles chloric acid, and is very unstable. The bromates when heated give off oxygen, and are converted into bromides.

Perbromic Acid, $HBrO_4$, is said by Kämmerer to be formed by the action of bromine on dilute perchloric acid, but its existence is doubtful.

No anhydrous oxide of bromine has yet been obtained.

Compounds of Iodine and Oxygen.

Two of these compounds are known, viz., iodic oxide, I_2O_5, and periodic oxide, I_2O_7. Both these are acid oxides, uniting with water and metallic oxides.

Hydrogen Iodate, or **Iodic Acid,** H_2O,I_2O_5, or HIO_3, may be prepared by the direct oxidation of iodine with nitric acid of specific gravity 1·5. Five parts of dry iodine with 200 parts of nitric acid are kept at a boiling temperature for several hours, or until the iodine has disappeared. The solution is then cautiously distilled to dryness, and the residue dissolved in water and made to crystallise.

Iodic acid is a very soluble substance, crystallising in colourless six-sided tables. At 107° it is resolved into water and iodic oxide, which forms tabular rhombic crystals, and when heated to the temperature of boiling olive oil, is completely resolved into iodine and oxygen. The solution of iodic acid is readily deoxidised by sulphurous acid. The iodates much resemble the chlorates: that of potassium is decomposed by heat into potassium iodide and oxygen gas.

Hydrogen Periodate, or **Periodic Acid,** H_2O,I_2O_7, or HIO_4.—When solution of sodium iodate is mixed with caustic soda, and a current of chlorine is passed through the liquid, two salts are formed —namely, sodium chloride and a sparingly soluble compound of sodium periodate with sodium hydroxide and water, $NaIO_4,NaHO,H_2O$, or $Na_2H_3IO_6$, the reaction taking place as represented by the equation—

$$NaIO_3 + 3NaHO + Cl_2 = 2NaCl + Na_2H_3IO_6.$$

This sodium salt is separated, converted into a silver salt, and dis-

solved in nitric acid: the solution yields, on evaporation, crystals of yellow silver periodate, from which the acid may be separated by the action of water, which resolves the salt into free acid and an insoluble basic periodate.

Periodic acid crystallises from its aqueous solution in deliquescent oblique rhombic prisms, which melt at 133°, and are resolved at 140° into oxygen, water, and iodic oxide.

The solution of periodic acid is reduced by many organic substances, and instantly by hydrochloric acid, sulphurous acid, and hydrogen sulphide. With hydrochloric acid it forms water, iodine chloride, and free chlorine. The metallic periodates are resolved by heat into oxygen and metallic iodides.

SULPHUR.

Symbol S. Atomic weight, 31·98. Vapour-density, 31·98.

SULPHUR occurs abundantly in nature both free and in combination. In the free state it is found in the neighbourhood of volcanos, both active and extinct, either in transparent yellow crystals or in opaque crystalline masses, and is separated from the rock or earth in which it is imbedded, by simple fusion. Large quantities of sulphur are thus obtained from Italy and Sicily.

Sulphur occurs, however, in still greater abundance in combination with metals, forming the *metallic sulphides*, *e.g.*, iron pyrites, FeS_2, copper pyrites, $CuFeS_2$, galena, PbS, cinnabar, HgS; or with metals and oxygen, forming *sulphates*, *e.g.*, gypsum, $CaSO_4,2H_2O$, heavy spar, $BaSO_4$, bitter spar, $MgSO_4,7H_2O$, &c.

Large quantities of sulphur are obtained by the distillation of iron pyrites, which is thereby resolved into a lower sulphide of iron and free sulphur, thus: $3FeS_2 = Fe_3S_4 + S_2$. Smaller quantities are obtained as a bye-product in the manufacture of coal-gas. The gas, as it issues from the retorts, contains hydrogen sulphide, and by passing it over oxide of iron, a sulphide of iron is formed, which, on exposure to the air, is oxidised, with separation of sulphur: $2FeS + O_3 = Fe_2O_3 + S_2$.

Lastly, sulphur may be obtained from the residue or waste of the soda-manufacture (see SODIUM) which consists of calcium sulphide mixed with chalk, lime, and alkaline sulphides. On exposing this mixture to the air, the calcium sulphide is partly oxidised to thiosulphate, CaS_2O_3, and on treating the resulting mass with hydrochloric acid, calcium chloride is formed and free sulphur is deposited:

$$2CaS + CaS_2O_3 + 6HCl = 4S + 3CaCl_2 + 3H_2O.$$

Properties.—Pure sulphur is a pale-yellow brittle solid, of well-known appearance. It melts when heated, and distils over un-

μερος, part). There are but few examples of this relation amongst inorganic compounds, but it is of frequent occurrence in organic chemistry. The *α*-modification, formed by cooling the liquid oxide, solidifies at +16° in long colourless prisms which melt at the same temperature; it boils at 46°; and its vapour at 20° has a tension represented by 200 millimeters of mercury. *β-Sulphuric oxide* is produced from the *α*-modification at temperatures below 25°; above 27° the transformation does not go on. It forms extremely fine white needles; at temperatures above 50° it gradually liquefies and passes into the first modification. Liquid sulphuric oxide undergoes very great expansion by heat, its mean coefficient of expansion between 25° and 45° being 0·0027 for 1° C., that is to say, more than two-thirds as great as that of gases. The two modifications differ greatly in their relations to solvents. Liquid sulphuric oxide mixes in all proportions with hydrogen sulphate, H_2SO_4; the *β*-oxide dissolves in sulphuric acid with extreme slowness, and gradually separates from a mixture of 10 parts SO_3 and 1–2 parts H_2SO_4. With a larger proportion of the acid, no solid oxide separates, even on cooling to a low temperature; if the proportion of acid, H_2SO_4, amounts to 5 parts for 10 parts of oxide, the mixture may deposit crystals of pyrosulphuric acid, $H_2S_2O_7$ or H_2SO_4,SO_3.

Sulphuric Acid, H_2SO_4.—The preparation of this important acid depends upon the fact that, when sulphurous oxide, nitrogen tetroxide, and water are present together in certain proportions, the sulphurous oxide becomes oxidised at the expense of the nitrogen tetroxide, which, by the loss of one-half of its oxygen, sinks to the condition of nitrogen dioxide. The operation is thus conducted:

A large and very long chamber is built of sheet-lead supported by timber framing; on the outside, at one extremity, a small furnace or oven is constructed, having a wide tube leading into the chamber. In this, sulphur is kept burning, the flame of which heats a crucible containing a mixture of nitre and oil of vitriol. A shallow stratum of water occupies the floor of the chamber, and a jet of steam is also introduced. Lastly, an exit is provided at the remote end of the chamber for the spent and useless gases. The effect of these arrangements is to cause a constant supply of sulphurous oxide, atmospheric air, nitric acid vapour, and water in the state of steam, to be thrown into the chamber, there to mix and react upon each other. The nitric acid immediately gives up a part of its oxygen to the sulphurous oxide, and is itself reduced to nitrogen tetroxide, N_2O_4 or NO_2; it does not remain in this state, however, but suffers further deoxidation until it becomes reduced to nitrogen dioxide, N_2O_2 or NO. That substance, in contact with free oxygen, absorbs a portion of the latter, and once more becomes tetroxide, which is again destined to undergo deoxidation by a fresh quantity of sulphurous oxide. A very small portion of nitrogen tetroxide mixed with atmospheric air and sulphurous oxide, may

thus in time convert an indefinite amount of the latter into sulphuric acid, by acting as a kind of carrier between the oxygen of the air and the sulphurous oxide. The presence of water is essential to this reaction, which may be represented by the equation,

$$NO_2 + SO_2 + H_2O = NO + H_2SO_4.$$

Such is the simplest view that can be taken of the production of sulphuric acid in the leaden chamber; but it is too much to affirm that it is strictly true; the reaction may be more complex. When a little water is placed at the bottom of a large glass globe, so as to maintain a certain degree of humidity in the air within, and sulphurous oxide and nitrogen tetroxide are introduced by separate tubes, symptoms of chemical action become immediately evident, and after a little time a white crystalline matter is observed to condense on the sides of the vessel. This substance appears to be a compound of sulphuric acid, nitrous acid, and a little water.* When thrown into water, it is resolved into sulphuric acid, nitrogen dioxide, and nitric acid. This body is certainly very often produced in large quantity in the leaden chambers; but that its production is indispensable to the success of the process, and constant when the operation goes on well and the nitrogen tetroxide is not in excess, may perhaps admit of doubt.

The water at the bottom of the chamber thus becomes loaded with sulphuric acid. When a certain degree of strength has been reached, the acid is drawn off and concentrated by evaporation, first in leaden pans, and afterwards in stills of platinum, until it attains a density (when cold) of 1·84, or thereabouts; it is then transferred to carboys, or large glass bottles fitted in baskets, for sale. This manufacture is one of great importance, and is carried on to a vast extent, the annual production in Great Britain amounting to no less than 850,000 tons.†

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* Gaultier de Claubry assigned to this substance the composition expressed by the formula $2(N_2O_3,2H_2O),5SO_3$, and this view has generally been received by recent chemical writers. De la Provostaye has since shown that a compound possessing all the essential properties of the body in question may be formed by bringing together, in a sealed glass tube, liquid sulphurous oxide and liquid nitrogen tetroxide, both free from water. The white crystalline solid soon begins to form, and at the expiration of twenty-six hours the reaction appears complete. The new product is accompanied by an exceedingly volatile greenish liquid, having the characters of nitrous acid. The white substance, on analysis, was found to contain the elements of two molecules of sulphuric oxide, and one of nitrous oxide, or $N_2O_3,2SO_3$. De la Provostaye explains the anomalies in the different analyses of the leaden-chamber product, by showing that the pure substance forms crystallisable combinations with different proportions of sulphuric acid. (Ann. Chim. Phys. lxxiii. 362.) See also Weber (Jahresbericht für Chemie, 1863, p. 738; 1865, p. 93; Bull. Soc. Chim. de Paris, 1867, i. 15.)

† For a fuller description of the process and figures of the apparatus, see Roscoe and Schorlemmer's Treatise on Chemistry, vol. i. pp. 319–338.

Sulphuric acid is now more frequently made by burning iron pyrites, or poor copper ore, or zinc-blende, instead of Sicilian sulphur: as thus prepared it very frequently contains arsenic, from which it may be freed, however, by heating it with a small quantity of sodium chloride, or by passing through the heated acid a current of hydrochloric acid gas, whereby the arsenic is volatilised as trichloride.

The most concentrated sulphuric acid, or *oil of vitriol*, as it is often called, is a definite combination of 40 parts sulphuric oxide and 9 parts of water, and is represented by the formula H_2O,SO_3 or H_2SO_4. It is a colourless oily liquid, having a specific gravity of about 1·85, of intensely acid taste and reaction. Organic matter is rapidly charred and destroyed by it. At the temperature of −26° C. (−15° F.) it freezes; at 327° C. (620° F.) it boils, and may be distilled without decomposition. Oil of vitriol has a most energetic attraction for water; it withdraws aqueous vapour from the air, and when it is diluted with water, great heat is evolved, so that the mixture always requires to be made with caution. Oil of vitriol is not the only hydrate of sulphuric oxide; three others are known to exist. When the fuming oil of vitriol of Nordhausen is exposed to a low temperature, a white crystalline substance separates, which is a hydrate containing half as much water as the common liquid acid. Further, a mixture of 98 parts of strong liquid acid and 18 parts of water, $2H_2O,SO_3$ or H_2SO_4,H_2O, congeals or crystallises at a temperature above 0° C., and remains solid even at 7·2° C. (45° F.) Lastly, when a very dilute acid is concentrated by evaporation in a vacuum over a surface of oil of vitriol, the evaporation stops when the sulphuric oxide and water bear to each other the proportion of 80 to 54, answering to the formula $3H_2O,SO_3$ or $H_2SO_4,2H_2O$.

When the vapour of sulphuric acid is passed over red-hot platinum, it is decomposed into oxygen and sulphurous acid. St. Claire Deville and Debray have recommended this process for the preparation of oxygen on the large scale, the sulphurous acid being easily separated by its solubility in water or alkaline solutions.

Sulphuric acid acts readily on metallic oxides; converting them into sulphates. It also decomposes carbonates with the greatest ease, expelling carbon dioxide with effervescence. With the aid of heat it likewise decomposes all other salts containing acids more volatile than itself. The sulphates are a very important class of salts, many of them being extensively used in the arts. Most sulphates are soluble in water, but they are all insoluble in alcohol. The barium, calcium, strontium, and lead salts are insoluble, or very slightly soluble, in water, and are formed by precipitating a soluble salt of either of those metals with sulphuric acid or a soluble metallic sulphate. Barium sulphate is quite insoluble in water: consequently sulphuric acid, or its soluble salts, may be detected readily by solution of barium nitrate or chloride: a white precipitate is thereby formed, which does not dissolve in nitric or *hydro*chloric acid.

Disulphuric or **Pyrosulphuric Acid**, $H_2S_2O_7$ (also called *Fuming Sulphuric Acid* and *Nordhausen Sulphuric Acid*).—This acid contains the elements of one molecule of sulphuric oxide and one molecule of sulphuric acid, or of two molecules of sulphuric acid *minus* one molecule of water:

$$H_2S_2O_7 = SO_3,H_2SO_4 = 2H_2SO_4 - H_2O.$$

It may be obtained of definite composition and in the crystalline form by adding liquid sulphuric oxide to strong sulphuric acid, in the proportion above indicated. The resulting crystals melt at 35°. It is also prepared from the impure ferric sulphate obtained by exposing ordinary ferrous sulphate (green vitriol) to a moderate heat in contact with the air. This ferric sulphate is distilled in earthen retorts arranged in a reverberatory furnace, and the distillate, consisting chiefly of sulphuric oxide, is received in a small quantity of water, or more frequently in ordinary strong sulphuric acid. A brown fuming liquid is thus obtained, which agrees nearly in composition with the formula $H_2S_2O_7$, has a specific gravity of 1·9, solidifies at 0° in colourless crystals, and is resolved at a gentle heat into SO_3 which distils over, and H_2SO_4 which remains behind.

The manufacture of fuming sulphuric acid in the manner just described was first practised at Nordhausen in Saxony, and appears to have been known since the fifteenth century; but it is now carried on almost exclusively in Bohemia. An easier and more productive method of obtaining the sulphuric oxide required for its formation is that of Messel and Squire, already described (p. 191). Fuming sulphuric acid was until lately employed only for dissolving indigo, but it is now used in very large quantities for dissolving anthraquinone for the manufacture of artificial alizarin. (See Organic Chemistry.)

The pyrosulphates, that of potassium, for example, which has the composition $K_2S_2O_7$, or K_2SO_4,SO_3, are prepared by the action of sulphuric oxide on the corresponding sulphates. When strongly heated, they give off sulphuric oxide, and are converted into sulphates.

Hyposulphurous Acid, H_2SO_2 (also called *Hydrosulphurous Acid*).—This acid is formed by the action of zinc on an aqueous solution of sulphurous acid. The zinc dissolves without evolution of hydrogen, merely removing an atom of oxygen. A yellow solution is thereby formed, which possesses much greater decolorising power than sulphurous acid itself, and quickly reduces the metals from salts of silver and mercury. This solution is, however, very unstable, and quickly loses its bleaching power. A more definite product is obtained by immersing clippings of zinc in a concentrated solution of acid sodium sulphite, $NaHSO_3$, contained in a closed vessel, whereby sodium hyposulphite, Na_2SO_2, and zinc-sodium sulphite, $Na_2Zn(SO_3)_2$, are produced, the latter crystallising out.

Tetrathionic Acid, $H_2S_4O_6$.—This acid was discovered by Fordos and Gelis. When iodine is added to a solution of barium thiosulphate, a large quantity of that substance is dissolved, and a clear colourless solution obtained, which, besides barium iodide, contains barium tetrathionate: $2BaS_2O_3 + I_2 = BaI_2 + BaS_4O_6$. By suitable means, the acid can be eliminated, and obtained in a state of solution. It very closely resembles dithionic acid. The same acid is produced by the action of sulphurous acid on chlorine disulphide.

Pentathionic Acid, $H_2S_5O_6$.—This acid was discovered by Wackenroder, who formed it by the action of hydrogen sulphide on sulphurous acid: $5H_2SO_3 + 5H_2S = H_2S_5O_6 + 9H_2O + S_5$. It is colourless and inodorous, of acid and bitter taste, and capable of being concentrated to a considerable extent by cautious evaporation.

Under the influence of heat, it is decomposed into sulphur, sulphurous and sulphuric acids, and hydrogen sulphide. The salts of pentathionic acid are nearly all soluble. The barium salt crystallises from alcohol in square prisms. The acid is also formed when lead dithionate is decomposed by hydrogen sulphide, and when chlorine monosulphide is heated with sulphurous acid.

Oxychlorides.—1. *Sulphurous Chloride*, $SOCl_2$.—This compound, also called *Chloride of Thionyl*, is derived from sulphurous acid, SO_3H_2 or $SO(HO)_2$, by the substitution of 2Cl for 2HO. It is formed by the action of water, alcohols, acids, &c., on the sulphides of chlorine; but is more easily prepared by the action of phosphorus pentachloride on sulphurous oxide, or by that of phosphorus oxychloride on calcium sulphite:

$$SO_2 + PCl_5 = POCl_3 + SOCl_2.$$
$$3CaSO_3 + 2POCl_3 = Ca_3P_2O_8 + 3SOCl_2.$$

It is separated by distillation from the fixed calcium phosphate produced simultaneously in the second, and by fractional distillation from the phosphorus oxychloride produced in the first reaction.

Sulphurous chloride is a colourless, strongly refracting liquid, which boils at 82°. It is decomposed by water, yielding hydrochloric and sulphurous acids; and by alcohols with formation of alcoholic chlorides and sulphurous acid, thus:

$$SOCl_2 + 2H_2O = 2HCl + H_2SO_3$$
$$SOCl_2 + \underset{\text{Ethyl alcohol.}}{2(C_2H_5)HO} = \underset{\text{Ethyl chloride.}}{2C_2H_5Cl} + H_2SO_3.$$

Sulphuric chloride, or *Sulphuryl chloride*, SO_2Cl_2 (also called *Chlorosulphuric acid*), is formed by prolonged exposure of a mixture of chlorine and sulphurous oxide gases to strong sunshine; also, together with phosphorus oxychloride, by the action of phosphorus pentachloride on sulphuric oxide:

$$SO_3 + PCl_5 = POCl_3 + SO_2Cl_2;$$

but it is best prepared by distilling strong sulphuric acid with the pentachloride, or lead sulphate with the oxychloride of phosphorus:

$$H_2SO_4 + 2PCl_5 = SO_2Cl_2 + 2POCl_3 + 2HCl$$
$$3PbSO_4 + 2POCl_3 = 3SO_2Cl_2 + Pb_3P_2O_8$$
Lead phosphate.

Sulphuric chloride is a colourless fuming liquid, of specific gravity 1·66. It boils at 77°, and may be distilled unchanged over caustic lime or baryta. When poured into water, it sinks in the form of oily drops, which gradually disappear, being converted into hydrochloric and sulphuric acids:

$$SO_2Cl_2 + 2H_2O = 2HCl + H_2SO_4.$$

With alcohol it behaves in a similar manner, thus:

$$SO_2Cl_2 + 2(C_2H_5)HO = 2C_2H_5Cl + H_2SO_4.$$

In the actual reaction, however, the sulphuric acid is converted into ethylsulphuric acid by the intervention of another atom of alcohol:

$$H_2SO_4 + (C_2H_5)HO = H_2O + (C_2H_5)HSO_4.$$

Sulphuric Hydroxychloride or **Chlorhydrate,** $HClSO_3$ or $SO_2(HO)Cl$ (also called *Chlorhydrosulphurous Acid* and *Sulphuric Chlorhydrin*).—This compound, discovered by Williamson, is intermediate in composition between sulphuric acid and sulphuric chloride, and is derived from sulphuric acid, SO_4H_2, or $SO_2(HO)_2$, by the substitution of 1Cl for 1HO. It is the first product of the action of phosphorus pentachloride on strong sulphuric acid:

$$SO_2(HO)(HO) + PCl_5 = POCl_3 + HCl + SO_2(HO)Cl.$$

As thus prepared it is mixed with sulphuric chloride; but it may be obtained pure by treating sulphuric acid with phosphorus oxychloride, hydrochloric and metaphosphoric acid being produced at the same time:

$$2SO_2(HO)(HO) + POCl_3 = 2SO_2(HO)Cl + HCl + HPO_3.$$

It is also formed by the action of water on sulphuric chloride:

$$SO_2Cl_2 + H_2O = HCl + HClSO_3.$$

Sulphuric hydroxychloride is a colourless liquid, which boils at about 150°, being at the same time partially resolved into sulphuric acid and sulphuric chloride: $2HClSO_3 = H_2SO_4 + Cl_2SO_2$. When poured into water, it sinks to the bottom and gradually dissolves, with formation of hydrochloric and sulphuric acids. It has decided acid properties, and forms definite salts in which its hydrogen is

replaced by metals. Thus it dissolves sodium chloride at a gentle heat, with evolution of hydrochloric acid, and formation of the salt $NaClSO_3$.

Pyrosulphuric Chloride, $S_2O_5Cl_2$ or $(SO_2Cl)_2O$.—This compound is formed on heating together phosphorus pentachloride and sulphuric oxide:

$$PCl_5 + 2SO_3 = S_2O_5Cl_2 + POCl_3,$$

and by the action of phosphorus pentachloride on sulphuric hydroxychloride:

$$PCl_5 + 2SO_2ClOH = (SO_2Cl)_2O + POCl_3 + 2HCl.$$

It is a colourless oily liquid of sp. gr. 1·819 at 18°, boiling at 146°. In contact with water it decomposes slowly and noiselessly, and is thus distinguished from sulphuric hydroxychloride, which is rapidly decomposed, with almost explosive violence, when thrown into water. When heated above its boiling point, it is resolved into chlorine, sulphurous oxide, and sulphuric oxide:

$$S_2O_5Cl_2 = SO_3 + SO_2 + Cl_2.$$

When submitted to the action of phosphorus pentachloride, it yields chlorine, sulphurous oxide, and phosphorus oxychloride:

$$S_2O_5Cl_2 + PCl_5 = POCl_3 + 2SO_2 + 2Cl_2.$$

SELENIUM.

Symbol, Se. Atomic weight, 79. Vapour-density, 79.

This substance, much resembling sulphur in its chemical relations, occurs frequently, associated in small quantities with that element, or replacing it in certain metallic combinations, as in the lead selenide of Clausthal in the Hartz. To separate it, the pulverised ore is treated with hydrochloric acid to dissolve earthy carbonates, and the washed and dried residue is ignited for some time with an equal quantity of black flux (a mixture of potassium carbonate and charcoal). The selenium is thereby converted into potassium selenide, which by treatment with boiling water is dissolved away from the oxides formed at the same time. This solution when exposed to the air absorbs oxygen, and yields the selenium as a grey deposit, which may be purified by washing, drying, and distillation.*

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* For further details, and for other methods, see Gmelin's Handbook *of Chemistry*, English edition, vol. ii. p. 232.

A new source of selenium has lately been discovered in the combustion of seleniferous pyrites for the manufacture of sulphuric acid, selenic oxide, SeO_3, being thereby formed, and reduced by sulphurous acid, in the course of the process, to free selenium, which partly dissolves in the sulphuric acid, and partly remains suspended. Now when this seleniferous sulphuric acid is used for the production of salt-cake in the soda-manufacture (see SODIUM CARBONATE), the selenium volatilises with the escaping hydrochloric acid, and is deposited in the first condensers, the deposit thus formed containing from 41 to 45 per cent. of selenium. To extract this selenium, the deposit suspended in water is treated with chlorine, whereby selenium tetrachloride is formed, which is then decomposed by the water, yielding selenious acid, partly oxidised to selenic acid. The dark-coloured liquid is then filtered through cloth, and boiled with excess of hydrochloric acid to reduce the selenic acid to selenious acid, which is then further reduced to selenium by the action of acid sodium sulphite. By this process large quantities of nearly pure selenium are easily and rapidly obtained.*

Selenium, like sulphur, exists in two allotropic modifications, one soluble, the other insoluble in carbon sulphide. *α.* The *soluble modification* is obtained as a finely divided brick-red powder on passing a current of sulphur dioxide into a cold solution of selenious acid,—and as a black crystalline powder when the same gas is passed through a hot solution of the acid. It crystallises from solution in carbon sulphide in small dark red monoclinic crystals, isomorphous with monoclinic sulphur, and having a specific gravity of 4·5. It has no definite melting point, but softens gradually when heated.—*β. Insoluble* or *Metallic Selenium* is obtained by quickly cooling melted selenium to 210°, and keeping the melted mass at this temperature for some time, whereupon it ultimately solidifies to a granular crystalline mass, the temperature then suddenly rising to 217°. The solid selenium thus obtained has a density of 4·5, and is insoluble in carbon sulphide. This metallic selenium melts constantly at 217°, and is converted by rapid cooling into the amorphous soluble variety. Both modifications dissolve in selenium chloride, the selenium separating therefrom in the metallic form. Selenium boils somewhat below 700°, forming a dark red vapour, which condenses either in the form of scarlet "flowers of selenium," or in dark shining drops.

The vapour-density of selenium, like that of sulphur, diminishes very rapidly as its temperature rises, being 110·7 (hydrogen being taken as unity) at 860°, and 81·5 at 1420°, which does not differ greatly from the theoretical density.

Metallic selenium conducts electricity, and its conducting power is increased by exposure to light, and diminished by heating. Exposure to diffused daylight immediately diminishes the electrical

* Bulletin de la Société chimique de Paris, 2me série, xxxvii. 443; Journal of the Chemical Society, xliv. 16.

resistance of selenium to one-half of what it was before, but on cutting off the light, the resistance slowly increases, and soon reaches its original amount.

Selenium when heated in the air burns with a pale blue flame, emitting an odour of decayed horse-radish, due to the formation of an oxide.

Hydrogen Selenide, H_2Se.—This compound, also called *Selenhydric acid* and *Selenietted hydrogen*, is formed by the action of dilute sulphuric acid on selenide of potassium or iron. It is very much like hydrogen sulphide, being a colourless gas, freely soluble in water, and decomposing metallic solutions, with formation of insoluble selenides. It acts very powerfully on the mucous membrane of the nose, exciting catarrhal symptoms and temporarily destroying the sense of smell.

Selenium Chlorides.—The *monochloride*, Se_2Cl_2, formed by passing chlorine gas over selenium, is a brown oily liquid, which readily dissolves selenium, and deposits it in the metallic form on cooling. It is slowly decomposed by water, yielding selenious acid, hydrochloric acid, and free selenium: $2Se_2Cl_2 + 3H_2O = H_2SeO_3 + 3Se + 4HCl$.

The *tetrachloride*, $SeCl_4$, is obtained by the further action of chlorine on the monochloride, or by heating the dioxide with phosphorus pentachloride: $3SeO_2 + 3PCl_5 = 3SeCl_4 + P_2O_5 + POCl_3$. It is a white solid body, which when heated volatilises without previous fusion, and sublimes in small crystals. It dissolves in water, forming hydrochloric and selenious acids: $SeCl_4 + 3H_2O = 4HCl + H_2SeO_3$.

Selenium Bromides.—The *monobromide*, Se_2Br_2, formed by heating together equal weights of bromine and selenium, is a black semi-opaque liquid, having a density of 3·6 at 15°. It smells like sulphur monochloride, and stains the skin brown-red. It is decomposed by heat and by the action of water, yielding in the latter case hydrobromic and selenious acids. The *tetrabromide*, $SeBr_4$, formed by the further action of bromine on the monobromide, is an orange-red crystalline powder, which volatilises without decomposition between 75° and 80°, and sublimes in black hexagonal scales. It smells like sulphur chloride, decomposes in moist air into bromine and the monobromide, and dissolves in excess of water, with formation of hydrobromic and selenious acids.

Selenium Iodides.—The *mono-iodide*, Se_2I_2, formed by direct combination, is a black shining crystalline body melting at 68—70°, with slight evolution of iodine. It is resolved into its elements at a higher temperature, and is decomposed by water like the corresponding chloride and bromide.—The *tetra-iodide*, SeI_4, is a dark-coloured *granular crystalline* mass, melting at 75—80° to a brownish-black

liquid, translucent in thin films. At a higher temperature it is resolved into its elements.

Fluoride.—This compound, formed by passing selenium vapour over melted lead fluoride, sublimes in crystals, which dissolve in hydrofluoric acid and are decomposed by water.

Oxides and Oxy-acids of Selenium.—Two oxides of selenium are known. The one containing the smaller proportion of oxygen is formed by the imperfect combustion of selenium in air or oxygen gas. It is a colourless gas, which is the source of the peculiar horse-radish odour above mentioned. Its composition is not known.

The higher oxide, SeO_2, called selenious oxide, is produced by burning selenium in a stream of oxygen gas. It is a white solid substance, which absorbs water rapidly, forming a hydroxide.

Selenious acid, H_2SeO_3 or H_2O,SeO_2.—This acid, analogous in composition and properties to sulphurous acid, is likewise produced by dissolving selenium in nitric or nitromuriatic acid. It is deposited from its hot aqueous solution by slow cooling in prismatic crystals like those of saltpetre; but when the solution is evaporated to dryness, the selenious acid is resolved into water and selenious oxide, which sublimes at a higher temperature.

Selenious acid is a very powerful acid, approximating to sulphuric acid in the energy of its reactions. It reddens litmus, decomposes carbonates with effervescence, and decomposes nitrates and chlorides with aid of heat. Its solution precipitates lead and silver salts, and is decomposed by hydrogen sulphide, yielding a precipitate of selenium sulphide: $H_2SeO_3 + 2H_2S = 3H_2O + SeS_2$.

The metallic selenites resemble the sulphites. When heated with sodium carbonate in the inner blow-pipe flame, they emit the characteristic odour of selenium. They are not decomposed by boiling with hydrochloric acid.

Selenic acid, H_2SeO_4, is analogous in composition to sulphuric acid. The corresponding anhydrous oxide is not known. Selenic acid is prepared by fusing potassium or sodium nitrate with selenium, precipitating the selenate so produced with a lead salt, and decomposing the resulting compound with hydrogen sulphide. The acid strongly resembles oil of vitriol; but when very much concentrated, it is decomposed by heat into selenious acid and oxygen. The selenates bear the closest analogy to the sulphates in almost every particular. They are decomposed by boiling with hydrochloric acid, with evolution of chlorine and formation of a metallic selenide.

TELLURIUM.

Symbol, Te. Atomic weight, 128. Vapour-density, 128.

THIS element possesses many of the characters of a metal, but it bears so close a resemblance to selenium, both in its physical properties and its chemical relations, that it is most appropriately placed in the same group with that body. Tellurium is found in a few scarce minerals, in association with gold, silver, lead, and bismuth, apparently replacing sulphur, and is most easily extracted from the bismuth sulpho-telluride of Chemnitz in Hungary The finely powdered ore is mixed with an equal weight of dry sodium carbonate, and the mixture, made into a paste with oil, is heated to whiteness in a closely covered crucible. Sodium telluride and sulphide are thereby produced, and metallic bismuth is set free. The fused mass is dissolved in water, and the solution freely exposed to the air, when the sodium and sulphur oxidise to sodium hydroxide and thiosulphate, while the tellurium separates in the metallic state.

Tellurium has the colour and lustre of silver; by fusion and slow cooling, it may be made to exhibit the form of rhombohedral crystals, similar to those of antimony and arsenic. It is brittle, and a comparatively bad conductor of heat and electricity; it has a density of 6·26, melts at a little below a red-heat, and volatilises at a higher temperature. Tellurium burns when heated in the air, and is oxidised by nitric acid.

Hydrogen Telluride, H_2Te.—*Tellurhydric Acid*, *Hydrotelluric Acid*, or *Telluretted Hydrogen*.—This compound is a gas, resembling sulphuretted and selenietted hydrogen. It is prepared by the action of hydrochloric acid on zinc telluride. It dissolves in water, forming a colourless liquid, which precipitates most metals from their solutions, and deposits tellurium on exposure to the air.

Tellurium Chlorides.—Tellurium forms a dichloride, $TeCl_2$, and a tetrachloride, $TeCl_4$, both volatile and decomposible by excess of water, the latter being completely resolved into tellurous and hydrochloric acids: $TeCl_4 + 3H_2O = 4HCl + H_2TeO_3$.

The tetrachloride unites with the chlorides of the alkali-metals, to form crystallisable double salts.

The *bromides* and *iodides of tellurium* correspond with the chlorides in properties and composition.

Oxides and Oxy-acids.—Tellurium forms two oxides, analogous in composition to the oxides of sulphur, and likewise forming acids by combination with water.

Tellurous Oxide, TeO_2, may be prepared by heating the *precipitated* acid to low redness. It also separates in semi-crystalline

grains from the aqueous solution of the acid when gently heated; more abundantly and in well-defined octohedrons from the solution of tellurous acid in nitric acid. It is fusible and volatile, slightly soluble in water, but does not redden litmus. When fused with alkaline hydroxides or carbonates, it forms tellurites.

Tellurous Acid is best obtained by decomposing tellurium tetrachloride with water. It may also be prepared by dissolving tellurium in nitric acid of sp. gr. 1·25, and pouring the solution, after a few minutes, into a large quantity of water. By either process it is obtained as a somewhat bulky precipitate, which, when dried over oil of vitriol, appears as a light, white, earthy mass, having a bitter metallic taste. It is slightly soluble in water, more easily soluble in alkalis and acids, the nitric acid solution alone being unstable. Sulphurous acid, zinc, phosphorus, and other reducing agents, precipitate metallic tellurium from the acidified solution of tellurous acid. Like selenious acid, it is decomposed by hydrogen sulphide and alkaline hydrosulphides, with formation of a dark brown tellurium sulphide, which dissolves readily in excess of alkaline hydrosulphide, forming a sulpho-tellurite.

Tellurous acid is a hydroxide in which the acid and basic tendencies are nearly balanced; in other words, the tellurium of the compound can replace the hydrogen of an acid to form tellurous salts, and the hydrogen can be replaced by the basylous metals to form metallic tellurites.

Tellurium Salts.	
$Te(SO_4)_2$	Sulphate.
$Te(NO_3)_4$	Nitrate.
$Te(C_2O_4)_2$	Oxalate.
$TeCl_4$	Chloride.

Tellurites.	
H_2TeO_3	Hydrogen tellurite.
K_2TeO_3	Potassium tellurite.
$HKTeO_3$	Hydrogen and potassium tellurite.
$H_3K(TeO_3)_2$	Trihydropotassic tellurite.

The tellurites of potassium, sodium, barium, strontium, and calcium, are formed by fusing tellurous oxide or acid with the carbonates of the several metals in the required proportions. These tellurites are all more or less soluble in water. The tellurites of the other metals, which are insoluble, are obtained by precipitation.

Compounds of tellurous oxide with the halogen acids are also known. When this oxide is exposed to the action of gaseous *hydrogen bromide* in a vessel cooled to $-14°$, the compound $TeO_2,3HBr$ is formed in groups of small nearly black scales resembling iodine. At 40° this compound gives off HBr, and is reduced to $TeO_2,2HBr$, which, when heated to 300°, is resolved into water and a yellow oxybromide: $TeO_2,2HBr = H_2O + TeOBr_2$; and at a still higher temperature this oxybromide is decomposed into the tetrabromide and tellurous oxide: $2TeOBr_2 = TeBr_4 + TeO_2$. The tetrabromide passes off in black vapours and crystallises on cooling in dark brown needles.

Tellurous oxide is decomposed by *hydriodic acid* at ordinary temperatures, but absorbs it at $-15°$, forming a compound which decomposes as the temperature rises. Tellurous oxide likewise absorbs anhydrous *hydrofluoric acid.*

Telluric Oxide and Acid.—To prepare telluric acid, equal parts of tellurous oxide and sodium carbonate are fused, and the product is dissolved in water; a little sodium hydroxide is added, and a stream of chlorine passed through the solution. The liquid is next saturated with ammonia, and mixed with solution of barium chloride, by which a white insoluble precipitate of barium tellurate is thrown down. This is washed and digested with a quarter of its weight of sulphuric acid, and diluted with water. The filtered solution gives, on evaporation in the air, large crystals of telluric acid, which have the composition, $H_2TeO_4,2H_2O$.

Crystallised telluric acid is freely, although slowly, soluble in water: it has a metallic taste, and reddens litmus-paper. The crystals give off their water of crystallisation at 100°, and the remaining acid, H_2TeO_4, when strongly heated, gives off more water, and yields the anhydrous oxide, TeO_3, which is then insoluble in water, and even in a boiling alkaline liquid. At the temperature of ignition, telluric oxide loses oxygen, and passes into tellurous oxide.

The tellurates of the alkali-metals are soluble in water, and are prepared by dissolving the required quantities of telluric acid and an alkaline carbonate in hot water. The other tellurates are insoluble, and are obtained by precipitation.

The composition of the alkaline tellurates is exhibited by the following formulæ:—

Neutral or Bipotassic tellurate	K_2TeO_4	or K_2O,TeO_3
Acid or Hydro-potassic tellurate	$HKTeO_4$	or $H_2O,K_2O,2TeO_3$
Quadracid or Trihydro-potassic tellurate. .	$HKTeO_4,H_2TeO_4$	or $3H_2O,K_2O,4TeO_3$
Anhydrous Quadritellurate	$K_2TeO_4,3TeO_3$	or $K_2O,4TeO_3$

Tellurium Sulphides.—Tellurium forms two sulphides, TeS_2 and TeS_3, analogous in composition to the oxides; they are obtained by the action of hydrogen sulphide on solutions of tellurous acid and telluric acid respectively. They are brown or black substances, which unite with metallic sulphides, forming salts called thiotellurites and thiotellurates.

NITROGEN.

Symbol, N. Atomic weight, 14·01. Density, 14·01.

NITROGEN* constitutes about four-fifths of the atmosphere, and enters into a great variety of combinations. It may be prepared by several methods. One of the simplest of these is to burn out the oxygen from a confined portion of air by phosphorus, or by a jet of hydrogen.

A small porcelain capsule is floated on the water of the pneumatic trough, and a piece of phosphorus is placed in it and set on fire. A bell-jar is then inverted over the whole, and suffered to rest on the shelf of the trough, so as to project a little over its edge. At first the heat causes expansion of the air of the jar, and a few bubbles are expelled, after which the level of the water rises considerably. When the phosphorus becomes extinguished by exhaustion of the oxygen, and time has been given for the subsidence of the cloud of finely divided snow-like phosphoric oxide which floats in the residual gas, the nitrogen may be transferred into another vessel, and its properties examined.

Fig. 117.

Prepared by the foregoing process, nitrogen is contaminated with a little vapour of phosphorus, which communicates its peculiar odour. A preferable method is to fill a porcelain tube with turnings of copper, or, still better, with the spongy metal obtained by reducing the oxide with hydrogen; to heat this tube to redness; and then pass through it a slow stream of atmospheric air, the oxygen of which is entirely removed, during its progress, by the heated copper.

When chlorine gas is passed into solution of ammonia, the latter substance, which is a compound of nitrogen with hydrogen, is decomposed; the chlorine combines with the hydrogen, and the nitrogen is set free, with effervescence. In this manner very pure nitrogen can be obtained. In making this experiment, it is necessary to stop short of saturating or decomposing the whole of the ammonia; otherwise there will be great risk of accident from the formation of an exceedingly dangerous explosive compound, produced by the contact of chlorine with an ammoniacal salt.

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* *i.e.*, Generator of nitre; also called *Azote*, from *a*, privative, and *ξωή*, life.

Another very easy and perfectly safe method of obtaining pure nitrogen is to decompose a solution of potassium nitrite with ammonium chloride (sal-ammoniac). The potassium nitrite is prepared by passing the red vapours of nitrous acid, obtained by heating dilute nitric acid with starch, into a solution of caustic potash. On boiling the resulting solution with sal-ammoniac, nitrogen gas is evolved, while potassium chloride remains in solution. The reaction is represented by the equation,

$$KNO_2 + NH_4Cl = KCl + 2H_2O + N_2.$$

Nitrogen is destitute of colour, taste, and odour; it is a little lighter than air, its density being 0·972. A litre of the gas at 0° C. and 760 mm. barometric pressure weighs 1·25658 gram. 100 cubic inches, at 60° F. and 30 inches barometer, weigh 30·14 grains. Nitrogen is incapable of sustaining combustion or animal life, although, like hydrogen, it has no positive poisonous properties; neither is it soluble to any notable extent in water or in caustic alkali; it is, in fact, best characterised by negative properties.

COMPOUNDS OF NITROGEN AND HYDROGEN.

Ammonia, NH_3.—When powdered sal-ammoniac is mixed with moist calcium hydrate (slaked lime), and gently heated in a glass flask, a large quantity of gaseous matter is disengaged, which must be collected over mercury, or by displacement, advantage being taken of its low specific gravity.

Ammonia gas thus obtained is colourless; it has a strong pungent odour, and possesses in an eminent degree those properties to which the term *alkaline* is applied; that is to say, it turns the yellow colour of turmeric to brown, that of reddened litmus to blue, and combines readily with acids, neutralising them completely. Under a pressure of 6·5 atmospheres at 15·5°, ammonia condenses to the liquid form. Water dissolves about 700 times its volume of this gas, forming a solution which in a more dilute state has long been known under the name of *liquor ammoniæ;* by heat a great part is again expelled. The solution is decomposed by chlorine, sal-ammoniac being formed, and nitrogen set free.

Ammonia has a density of 0·589; a litre weighs 0·76271 gram. It cannot be formed by the direct union of its elements, although it is sometimes produced under rather remarkable circumstances by the deoxidation of nitric acid.* The great sources of ammonia are the feebly compounded azotised principles of the animal and vegetable kingdoms, which, when left to putrefactive change, or sub-

* A mode of converting the nitrogen of the atmosphere into ammonia, by a succession of chemical operations, will be noticed in connection with Cyanogen under Organic Chemistry.

jected to destructive distillation, almost invariably give rise to an abundant production of this substance.

The analysis of ammonia gas is easily effected. When a portion is confined in a graduated tube over mercury, and electric sparks are passed through it for a considerable time, the volume of the gas gradually increases until it becomes doubled. On examination, the tube is found to contain a mixture of 3 measures of hydrogen gas and 1 measure of nitrogen. Every two volumes of the ammonia, therefore, contained three volumes of hydrogen and one of nitrogen, the whole being condensed to one half. The weight of the two constituents is in the proportion of three parts hydrogen to 14 parts nitrogen.

Ammonia may also be decomposed into its elements by transmission through a red-hot tube.

The aqueous solution of ammonia is a very valuable reagent, and is employed in a great number of chemical operations, for some of which it is necessary to have it perfectly pure. The best mode of preparation is the following:—

Equal weights of sal-ammoniac (NH_4Cl), and quicklime (CaO), are taken; the lime is slaked in a covered basin, and the salt reduced to powder. These are mixed and introduced into a large flask connected with a wash-bottle and a receiver containing water. A little water is added to the mixture, just enough to damp it and cause it to aggregate into lumps. On cautiously applying heat to the flask, ammonia is disengaged very regularly and uniformly, and condenses in the water of the receiver. Calcium chloride ($CaCl_2$), with excess of calcium hydroxide (slaked lime) remains in the flask.

The decomposition of the salt is represented by the equation—

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

Solution of ammonia should be perfectly colourless, leave no residue on evaporation, and when supersaturated by nitric acid, give no cloud or muddiness with silver nitrate. Its density diminishes as its strength increases, that of the most concentrated being about 0·875. The value in alkali of any sample of *liquor ammoniæ* is however most safely inferred, not from a knowledge of its density, but from the quantity of acid a given amount will saturate.

When solution of ammonia is mixed with acids, salts are generated exactly analogous to the corresponding potassium and sodium compounds: they will be discussed in connection with the latter. The ammonia salts may be regarded either as direct compounds of ammonia, NH_3, with acids (HCl, for example), or as resulting from the replacement of the hydrogen of an acid by the group NH_4, called *ammonium*, which in this sense is a compound metal, chemically equivalent to potassium, sodium, silver, &c. Thus:—

Ammonia hydrochloride	NH_3,HCl	$= NH_4Cl$	Ammonium	chloride
,, nitrate	NH_3,HNO_3	$= NH_4NO_3$	,,	nitrate
,, sulphate	$(NH_3)_2,H_2SO_4$	$= (NH_4)_2SO_4$	,,	sulphate

The formulæ in the second column are exactly analogous to those of the potassium salts, KCl, KNO_3, K_2SO_4.

The aqueous solution of ammonia may be supposed to contain *ammonium hydroxide*, $NH_4.HO$; but this compound is not known in the solid state.

Any ammoniacal salt can at once be recognised by the evolution of ammonia which takes place when it is heated with slaked lime, or solution of potash or soda.

Hydroxylamine, NH_3O.—This compound, intermediate in composition between ammonia, NH_3, and ammonium hydroxide, $NH_4.HO$, is formed by the direct union of hydrogen with nitrogen dioxide: $NO + H_3 = NH_3O$, and may be prepared by passing nitrogen dioxide through a series of flasks in which hydrogen is evolved by heating hydrochloric acid with tin. The resulting liquid is freed from tin by hydrogen sulphide; the filtered liquid evaporated to dryness; the residue washed with cold alcohol, and digested with boiling alcohol; the alcoholic solution mixed with platinic chloride to precipitate sal-ammoniac; and the filtered alcoholic liquid mixed with ether, which throws down pure hydrochloride of hydroxylamine.

Hydroxylamine is also formed by the action of hydrogen (evolved as above) on nitric acid or ethyl nitrate:

$$NO_3H + 6H = 2H_2O + NH_3O.$$

Hydroxylamine is a very volatile and easily decomposible base, and can be obtained only in solution. Its salts are decomposed by potash, with evolution of nitrogen and formation of ammonia, quickly in concentrated, gradually in dilute solutions. Solutions of hydroxylamine may, however, be obtained by decomposing the salts in other ways, an alcoholic solution, for example, by decomposing the nitrate dissolved in alcohol with alcoholic potash. Alkaline carbonates also separate hydroxylamine, with evolution of carbon dioxide. The solutions have an alkaline reaction, and precipitate many metallic salts; with the salts of lead, iron, nickel, and zinc, and with chrome-alum and common alum, they form precipitates insoluble in excess of hydroxylamine. With aqueous cupric sulphate, hydroxylamine forms a grass-green precipitate, which, when boiled with water, is reduced, with evolution of gas, to cuprous oxide; an ammoniacal cupric solution is decolorised by it. Mercuric chloride is reduced to mercurous chloride, and if the hydroxylamine is in excess, to metallic mercury. Silver solutions yield a black precipitate, which is quickly reduced, with evolution of gas, to metallic silver. Hydroxylamine also reduces acid potassium chromate. In many of these reactions the hydroxylamine appears to be completely decomposed, with formation of nitrogen or its monoxide.

The salts of hydroxylamine decompose when heated, with copious and sudden evolution of gas; most of them easily form super-

saturated solutions; none of those yet examined contain water of crystallisation. The *hydrochloride*, NH_3O,HCl, crystallises from alcohol in long spicular crystals resembling urea; from water in large irregular six-sided tables; it melts at 100°, and then decomposes, with violent evolution of gas, into nitrogen, hydrochloric acid, water, and sal-ammoniac. The *nitrate*, NH_3O,HNO_3, solidifies slowly by spontaneous evaporation to a radio-crystalline, very deliquescent mass, easily soluble in absolute alcohol, decomposing at 100°.

Compounds of Nitrogen with the Halogen Elements.

Nitrogen and Chlorine.—When sal-ammoniac or ammonia nitrate is dissolved in water, and a jar of chlorine is inverted in the solution, the gas is absorbed, and a deep yellow oily liquid is observed to collect upon the surface of the solution, ultimately sinking in globules to the bottom. This is nitrogen chloride, one of the most dangerously explosive substances known. The following is the safest method of conducting the experiment:—

A somewhat dilute and tepid solution of pure sal-ammoniac in distilled water is poured into a clean basin, and a bottle of chlorine, the neck of which is quite free from grease, inverted in it. A shallow and heavy leaden cup is placed beneath the mouth of the bottle to collect the product. When enough has been obtained, the leaden vessel may be withdrawn with its dangerous contents, the chloride remaining covered with a stratum of water. The operator should protect his face with a strong wire-gauze mask when experimenting upon this substance.

The change may be explained by the equation—

$$NH_4Cl + 6Cl = NCl_3 + 4HCl.$$

Nitrogen chloride is very volatile, and its vapour is exceedingly irritating to the eyes. It has a specific gravity of 1·653. It may be distilled at 71°, although the experiment is attended with great danger. Between 93° and 105° it explodes with fearful violence. Contact with almost any combustible matter, as oil or fat of any kind, determines the explosion at common temperatures, a vessel of porcelain, glass, or even of cast-iron, being broken by it to pieces, and the leaden cup receiving a deep indentation. This body has usually been supposed to have the composition NCl_3, but recent experiments upon the corresponding iodine compound induce a belief that it contains hydrogen, and may perhaps be represented by the formula $NHCl_2$ or NH_2Cl.

Nitrogen and Iodine.—When finely powdered iodine is added to caustic ammonia, it is in part dissolved, giving a deep-brown solution, and the residue is converted into a black powder, called nitrogen iodide. The brown liquid consists of hydriodic acid holding iodine in solution, and is easily separated from the solid product by a filter. The latter, while still wet, is distributed in

are readily absorbed by water: this character is sufficient to distinguish it from all other gaseous bodies. A lighted taper plunged into the gas is extinguished; lighted phosphorus, however, burns in it with great brilliancy.

The specific gravity of nitrogen dioxide is 1·039; a litre weighs 1·34343 grams. It contains equal measures of oxygen and nitrogen gases united without condensation. When this gas is passed into the solution of a ferrous salt, it is absorbed in large quantity, and a deep brown, or nearly black liquid produced, which seems to be a definite compound of the two substances (p. 215). The compound is decomposed by boiling.

Nitrogen Trioxide, or **Nitrous Oxide**, N_2O_3.—When four measures of nitrogen dioxide are mixed with one measure of oxygen, and the gases, perfectly dry, are exposed to a temperature of $-18°$, they condense to a thin mobile blue liquid, which emits orange-red vapours.

Nitrogen trioxide, sufficiently pure for most purposes, is obtained by pouring concentrated nitric acid on lumps of arsenious acid, and gently warming the mixture, in order to start the reaction. The trioxide is then evolved as an orange-red gas, arsenic acid remaining behind.

Nitrous Acid, $HNO_2 = HO.NO$, is obtained as a beautiful blue liquid on dissolving the trioxide in ice-cold water: $N_2O_3 + H_2O = 2HNO_2$. It is very unstable, even at ordinary temperatures, decomposing into nitric acid, nitrogen dioxide, and water, $3HNO_2 = HNO_3 + N_2O_2 + H_2O$. In consequence of this instability of the acid, the metallic nitrites cannot be obtained by treating the aqueous solution of the acid with metallic oxides, but they may be formed in other ways: potassium nitrite, for example, may be obtained by fusing the corresponding nitrate, whereby a third part of the oxygen is driven off; and a solution of potassium or sodium nitrite may be prepared by passing the vapour of nitrogen trioxide—obtained as above by heating nitric acid with arsenious oxide (or with starch)—into a solution of caustic potash or soda.

Nitrosyl Chloride or *Nitrous Chloride*, NOCl, the chlorine-analogue of nitrous acid, is formed by direct union of chlorine and nitrogen dioxide, and by the action of phosphorus pentachloride on potassium nitrite: $PCl_5 + NO.OK = NO.Cl + KCl + POCl_3$; also, together with free chlorine, when a mixture of nitric and hydrochloric acids (*aqua regia*) is slowly heated:

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

Nitrosyl chloride in the pure state is an orange-yellow gas, which at the temperature of a freezing mixture, condenses to a deep orange-coloured limpid liquid, boiling at about $-8°$. It unites with many metallic chlorides, and is decomposed by basic oxides, yielding a nitrite and a chloride: *e.g.*,

$$NOCl + 2KOH = KNO_2 + KCl + H_2O.$$

Nitrosyl Bromide, NOBr, formed by passing nitrogen dioxide into bromine at $-7°$ to $-15°$, is a blackish-brown liquid, which begins to decompose at $-2°$, giving off nitrogen dioxide. If the temperature is allowed to rise to $+ 20°$, a dark brownish-red liquid remains, consisting of *nitrosyl tribromide*, $NOBr_3$, which is also formed when bromine is saturated with nitrogen dioxide at ordinary temperatures. It volatilises undecomposed when quickly heated, but is resolved by slow heating into bromine and nitrogen dioxide.

Nitrogen Tetroxide, N_2O_4 or NO_2, also called *Nitric Peroxide*.—This is the principal constituent of the deep red fumes always produced when nitrogen dioxide escapes into the air.

It may be obtained in the pure state:—1. By exposing a mixture of 2 vols. nitrogen dioxide and 1 vol. oxygen incorporated by passing through a tube filled with broken porcelain, and thoroughly dried by transmission over pumice soaked in oil of vitriol and then over recently fused stick potash, to the action of a freezing mixture of salt and ice; the tetroxide then condenses in transparent crystals, or if the slightest trace of moisture is present, into an almost colourless liquid. 2. By the direct combination of oxygen with the trioxide, as when a stream of oxygen is passed into the mixture of the trioxide and other oxides of nitrogen evolved by the action of fuming nitric acid on arsenious acid. The liquid tetroxide thus obtained is pure enough for most purposes after one distillation. 3. By heating thoroughly dried lead nitrate in a retort, whereby a mixture of the tetroxide and oxygen is evolved, the former of which may be condensed as above, while the latter passes on:

$$(NO_3)_2Pb = PbO + O + N_2O_4.$$

The first portions of nitrogen tetroxide thus obtained do not solidify, doubtless owing to the presence of a trace of moisture; but if the receiver be changed in the midst of the operation, and if every care has been taken to avoid moisture, the later portions may be obtained in the crystalline form.

Nitrogen tetroxide at very low temperatures forms transparent, colourless, prismatic crystals which melt at $-9°$, but when once melted do not resolidify till cooled down to $-30°$. Above $-9°$ it forms a mobile liquid of specific gravity 1·451, the appearance of which varies greatly according to the temperature. When still liquid below $-9°$, it is almost colourless; at $-9°$ it has a perceptible greenish-yellow tint; at $0°$ the colour is somewhat more marked; at $+10°$ it is decidedly yellow; and at $15°$ and upwards, orange-yellow, the depth of colour increasing progressively with the temperature up to $22°$, the boiling point of the liquid. The vapour has a brown-red colour, the depth of which also increases with the temperature, until at $40°$ it is so dark as to be almost opaque. This remarkable change of colour is accompanied by a great diminution of density as the temperature rises, both phenomena pointing to a molecular change produced in the vapour by heat. Playfair and Wanklyn

tact with the oxygen, is very considerable. Liebig's method combines great accuracy with unusual rapidity and facility of execution.

Fig. 119.

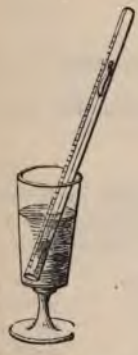
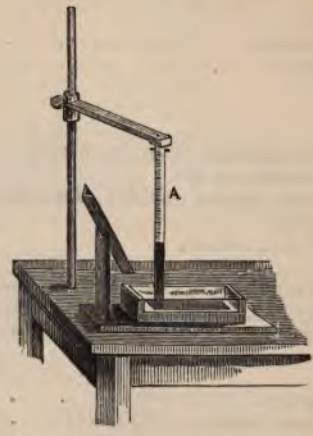


Fig. 120.



Another plan is to mix the air with hydrogen and pass an electric spark through the mixture: after explosion the volume of gas is read off and compared with that of the air employed. Since the analysis of gaseous bodies by explosion is an operation of great importance, it may be worth while to describe the process in detail, as it is applicable, with certain obvious variations, to a number of analogous cases.

Instruments for this purpose are called eudiometers. The simplest, and, on the whole, the most convenient, consists of a straight graduated glass tube (fig. 120) closed at the top, and having platinum wires inserted near the closed end, to give passage to an electric spark. This tube is filled with mercury, and inverted in a mercurial pneumatic trough.

For the analysis of air, a quantity sufficient to fill about one-sixth of the tube is introduced, and its volume accurately ascertained by reading off with a telescope the number of divisions on the tube to which the mercury reaches, whilst the height of the column of mercury in the tube above the trough, together with that of the barometer, and the temperature of the air, are also read off. A quantity of pure hydrogen gas is now added, more than sufficient to unite with all the oxygen present (about half the volume of the air), and the volume of the gas and the pressure exerted upon it, are determined as before. An electric spark is now passed through the *mixture,* care being taken to prevent any escape, by pressing the

open end of the eudiometer against a piece of sheet caoutchouc under the mercury in the trough. After the explosion, the volume is again determined, and is found to be less than that before the explosion. The volume of gas read off must in each case be reduced to standard pressure and temperature by the method already given (p. 40).

Now, since the hydrogen is in excess, and 2 volumes of that gas unite with 1 volume of oxygen to form water, one-third of the diminution must be the volume of the oxygen contained in the air introduced. An example will render this clear:—

Air introduced	100 measures.
Air and hydrogen	160
Volume after explosion	97
Diminution	63

$$\frac{63}{3} = 21 = \text{oxygen in the 100 measures.}$$

Nitrogen with Sulphur and Selenium.

Nitrogen Sulphide, N_2S_2, is obtained, together with other compounds, by the action of dry ammonia on sulphur monochloride or on thionyl chloride (pp. 188, 198), as a yellow powder which crystallises from carbon sulphide in yellowish-red rhombic prisms. It becomes dark-coloured at 120°, and emits pungent vapours; sublimes at 135° in yellowish-red crystals; begins to melt and give off gas at 158°; decomposes rapidly at 160°, and detonates violently when struck.

On adding sulphur monochloride, S_2Cl_2, to a solution of nitrogen sulphide in carbon sulphide, a yellow crystalline substance is formed, consisting of the compound N_2S_2,S_2Cl_2, which sublimes in needles when heated. On further addition of nitrogen sulphide, this yellow body is changed into a red compound $(N_2S_2)_2S_2Cl_2$, and this again, on still further addition, into $(N_2S_2)_3S_2Cl_2$, which forms a yellow powder permanent in the air.

Nitrogen Selenide, N_2Se_2, formed by the action of ammonia on selenium tetrachloride, is an orange-yellow mass which detonates strongly when heated to 200° or subjected to slight pressure.

Dinitrososulphuric Acid, $H_2SO_3(NO)_2$.—The alkali-salts of this acid (sulphuric acid, H_2SO_4, having 1 atom of oxygen replaced by 2 atoms of univalent nitrosyl, NO) are formed on passing nitrogen dioxide into the solution of an alkaline sulphite. They are colourless and crystalline, and are decomposed by all acids, even by carbonic acid, into sulphates and nitrogen monoxide, $K_2SO_3(NO)_2 = K_2SO_4 + N_2O$. The free acid (hydrogen salt) is not known. The

potassium salt is resolved by heat into potassium sulphite, K_2SO_3, and nitrogen dioxide, N_2O_2.

Nitrosulphonic acid, NO_2,SO_2,OH.*—This is the composition of the lead-chamber crystals, formed during the manufacture of sulphuric acid, when the supply of steam is insufficient to form that acid at once (p. 193). The same compound is formed by the action of strong nitric acid on sulphurous oxide: $SO_2 + NO_2.OH = NO_2.SO_2.OH$; by passing vapour of nitrosyl chloride into sulphuric acid: $NOCl + HO.SO_2.OH = HCl + NO_2.SO_2.OH$; and together with nitric acid by the action of nitrogen tetroxide on sulphuric acid: $N_2O_4 + HO.SO_2.OH = NO_2.OH + NO_2.SO_2.OH$. It crystallises in rhombic prisms, or in tabular or nodular masses, which begin to melt and give off vapour at 30°. It dissolves in small quantities of cold water, forming a blue liquid containing sulphuric and nitrous acids: $NO_2.SO_2.OH + HOH = HO.SO_2.OH + NO_2H$. It dissolves also in strong sulphuric acid, forming a solution which can be distilled without decomposition.

Nitrosulphonic chloride, $NO_2.SO_2.Cl$, formed by direct combination of SO_2 and NO_2Cl, is a white crystalline mass which melts when heated, with separation of nitrosyl chloride, and is decomposed by water, yielding sulphuric, hydrochloric, and nitrous acids.

Nitrosulphonic oxide or anhydride, $N_2S_2O_9 = (NO_2.SO_2)_2O$, is formed by the action of heat on nitrosulphonic acid, but is best prepared by passing dry nitrogen dioxide into sulphuric oxide, and heating the resulting solution nearly to the boiling point: $3SO_2O + N_2O_2 = (NO_2.SO_2)_2O + SO_2$. It is also formed by the action of sulphurous oxide on nitrogen tetroxide, and by heating the following compound. It crystallises in hard colourless square prisms, melting at 217°, to a yellow liquid which becomes darker at a higher temperature, and distils unchanged at 360°. It dissolves readily in strong sulphuric acid, forming nitrosulphonic acid.

Oxynitrosulphonic anhydride, $\left\{\begin{matrix} NO_2.SO_2 \\ ONO_2.SO_2 \end{matrix}\right\}O$, is formed when sulphuric oxide and nitrogen tetroxide are brought together at a low temperature, and separates as a white crystalline mass, which gives off oxygen when heated, and is reduced to the preceding compound.

Nitroxypyrosulphuric acid, $SO_3H.O.SO_3(NO_2)$, separates out at a certain degree of concentration from the thick oily liquid formed on mixing sulphuric oxide with nitrogen tetroxide. It dissolves in warm dilute nitric acid, and separates on cooling in crystals containing 1 molecule of water.

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* The name "sulphonic acid" is applied to derivatives of unsymmetrical sulphurous acid, $H.SO_2.OH$, formed by replacing the first hydrogen-atom by a univalent radicle: *e.g.*, methylsulphonic acid, $CH_3.SO_2.OH$; phenylsulphonic acid, $C_6H_5.SO_2.OH$.—(See ORGANIC CHEMISTRY.)

Ammon-sulphonic Acids.—The acids of this series, known only as potassium salts, are formed on the type NH_5 (the nitrogen being quinquivalent as in the nitrates). *Potassium ammon-tetrasulphonate*, $NH(SO_3K)_4$, is obtained as a crystalline precipitate on adding potassium sulphite in excess to a solution of the nitrite, potassium hydroxide remaining dissolved :

$$4K_2SO_3 + KNO_2 + 3H_2O = NH(SO_3K)_4 + 5KOH.$$

By prolonged contact with water, or by boiling with dilute potash-ley, this salt is resolved into acid potassium sulphate and *potassium ammontrisulphonate*, according to the equation, $NH(SO_3K)_4 + H_2O = KHSO_4 + NH_2(SO_3K)_3$. The trisulphonate separates in needle-shaped crystals, insoluble in cold water, but soluble in hot dilute potash, from which it may be recrystallised. By boiling with acidulated water it is converted into *ammon-disulphonate ;* thus :

$$NH_2(SO_3K)_3 + H_2O = HKSO_4 + NH_3(SO_3K)_2.$$

This last salt forms six-sided prisms, and is decomposed by prolonged boiling with a dilute acid, or by heating in the dry state at 200°, yielding ammonia, sulphurous oxide, and dipotassic sulphate : $NH_3(SO_3K)_2 = NH_3 + SO_2 + K_2SO_4$.

Hydroxylamine-disulphonic acid, $N(OH)(SO_3H)_2$ (also called *Sulph-azotic acid*), is formed, as potassium salt, by mixing the solutions of potassium nitrite and sulphite in the proportion of one molecule of the first to less than four molecules of the second. This salt crystallises in long bright transparent needles, and is converted by boiling with water into *potassium hydroxylaminemonosulphonate :*

$$N(OH)(SO_3K)_2 + H_2O = HKSO_4 + NH(OH)(SO_3K),$$

which may be crystallised from solution in hot water, but is decomposed by boiling with potash into ammonia, potassium sulphate, and nitrogen monoxide ; thus :

$$4NH(OH)(SO_3K) + 4KOH = N_2O + 2NH_3 + 4K_2SO_4 + 3H_2O.$$

PHOSPHORUS.

Symbol, P. Atomic weight, 30·96. Vapour-density, 61·92.

Phosphorus in the state of phosphoric acid is contained in the ancient unstratified rocks and in lavas of modern origin. As these disintegrate and crumble down into fertile soil, the phosphates pass into the organism of plants, and ultimately into the bodies of the animals to which the plants serve for food. The earthy phosphates play a very important part in the structure of the animal

frame, by communicating stiffness and inflexibility to the bony skeleton.

Phosphorus was discovered in 1669 by Brandt, of Hamburg, who prepared it from urine. The following is an outline of the method of preparation now adopted:—Thoroughly calcined bones are reduced to powder, and mixed with two-thirds of their weight of sulphuric acid diluted with a considerable quantity of water: this mixture, after standing for some hours, is filtered, and the nearly insoluble calcium sulphate is washed. The liquid is then evaporated to a syrupy consistence and mixed with charcoal powder, and the desiccation is completed in an iron vessel exposed to a high temperature. The residue, when quite dry, is transferred to a stoneware retort to which a wide bent tube is luted, dipping a little way into the water contained in the receiver (fig. 121). A narrow tube serves to give issue to the gases, which are conveyed to a chimney. This manufacture is now conducted on a very large scale, the consumption of phosphorus, for the apparently trifling article of instantaneous-light matches, being something prodigious.

Fig. 121.

Phosphorus, when pure, very much resembles in appearance imperfectly bleached wax, and is soft and flexible at common temperatures. Its density is 1·77, and that of its vapour 4·35, air being unity, or 61·92 referred to hydrogen as unity. It melts at 44°, and boils at 280°. On slowly cooling melted phosphorus, well-formed dodecahedrons are sometimes obtained. Phosphorus is insoluble in water, and is usually kept immersed in that liquid, but dissolves in oil, in native naphtha, and especially in carbon bisulphide. When set on fire in the air, it burns with a bright flame, generating phosphoric oxide. It is exceedingly inflammable, sometimes taking fire at the heat of the hand, and demands great care in its management; a blow or hard rub will very often kindle it. A stick of phosphorus held in the air always appears to emit a whitish smoke, luminous in the dark. This effect is chiefly due to a slow combustion which the phosphorus undergoes by the oxygen of the air, and upon it depends one of the methods employed for the analysis of air, as already described. It is singular that the slow oxidation of phosphorus may be entirely prevented by the presence of a small quantity of olefiant gas, or the vapour of ether, or some essential oil; phosphorus may even be distilled in an atmosphere containing vapour of oil of turpentine in considerable quantity. Neither does the action go on in pure oxygen—at least, at the temperature of 15·5°, which is very remarkable; but if the gas be rarefied, or diluted with nitrogen, hydrogen, or carbonic acid, oxidation is set up.

A very remarkable modification of this element is known by the name of amorphous phosphorus. It was discovered by Schrötter, and may be made by exposing common phosphorus for fifty hours at a temperature of 240° to 250°, in an atmosphere which is unable to act chemically upon it. At this temperature it becomes red and opaque, and insoluble in carbon bisulphide, whereby it may be separated from ordinary phosphorus. It may be obtained in compact masses when common phosphorus is kept for a week at a constant high temperature. It is a coherent, reddish-brown, infusible substance, of specific gravity between 2·089 and 2·106. It does not become luminous in the dark until the temperature is raised to about 200°, nor has it any tendency to combine with the oxygen of the air. When heated to 260°, it is reconverted into ordinary phosphorus.

When phosphorus is melted beneath the surface of hot water, and a stream of oxygen gas is forced upon it from a bladder, combustion ensues, and the phosphorus is converted in great part into a brick-red powder, which was formerly believed to be a peculiar oxide of phosphorus; but Schrötter has shown that it is a mixture consisting chiefly of amorphous phosphorus.

Phosphorus and Hydrogen.

Phosphorus Trihydride.—*Phosphine.*—*Phosphoretted Hydrogen*, PH_3.—This body is analogous in some of its chemical relations to ammonia gas; its alkaline properties are, however, much weaker.

It may be obtained in a state of purity by heating phosphorous acid in a small retort, the acid being then resolved into phosphine and phosphoric acid:

$$4H_3PO_3 = PH_3 + 3H_3PO_4.$$

Thus obtained, the gas has a density of 1·20 (referred to air), or 16·98 (referred to hydrogen), which number is the half of its molecular weight. It contains three volumes of hydrogen and half a volume of phosphorus vapour, condensed into two volumes. It has a highly disagreeable odour of garlic, is slightly soluble in water, and burns with a brilliant white flame, forming water and phosphoric acid.

Phosphine may also be produced by boiling together, in a retort of small dimensions, caustic potash or slaked lime, water, and phosphorus; the vessel should be filled to the neck, and the extremity of the latter made to dip into the water of the pneumatic trough. In the reaction which ensues, the water is decomposed, and both its elements combine with the phosphorus.

$$P_3 + 3CaH_2O_2 + 6H_2O = 2PH_3 + 3CaH_4P_2O_4$$

Calcium hydroxide. — Calcium hypophosphite.

The phosphine prepared by the latter process has the singular property of spontaneous inflammability when admitted into the air or into oxygen gas; with the latter, the experiment is very beautiful, but requires caution: the bubbles should be admitted singly. When kept over water for some time, the gas loses this property, without otherwise suffering any appreciable change; but if dried by calcium chloride, it may be kept unaltered for a much longer time. Paul Thénard has shown that the spontaneous combustibility of the gas arises from the presence of the vapour of a liquid hydrogen phosphide, PH_2, which may be obtained in small quantity, by conveying the gas produced by the action of water on calcium phosphide through a tube cooled by a freezing mixture. This substance forms a colourless liquid of high refractive power and very great volatility. It does not solidify at 0° F. (− 17·8° C.). In contact with air it inflames instantly, and its vapour in very small quantity communicates spontaneous inflammability to pure phosphine, and to all other combustible gases. It is decomposed by ight into gaseous phosphine, and a solid phosphide, P_2H, which is often seen on the inside of jars containing gas which, by exposure to light, has lost the property of spontaneous inflammation. Strong acids occasion its instantaneous decomposition. It is as unstable as hydrogen dioxide. It is to be observed that pure phosphine gas itself becomes spontaneously inflammable if heated to the temperature of boiling water.

Phosphine decomposes several metallic solutions, giving rise to precipitates of insoluble phosphides. With hydriodic acid it forms a crystalline compound, PH_4I, somewhat resembling sal-ammoniac.

Phosphorus and Chlorine.

Phosphorus forms two chlorides, analogous in composition to the oxides, the quantities of chlorine combined with the same quantity of phosphorus being in the proportion of 3 to 5.

Phosphorus Trichloride, or **Phosphorous Chloride**, PCl_3, is prepared in the same manner as sulphur dichloride, by gently heating phosphorus in dry chlorine gas, the phosphorus being in excess; or by passing the vapour of phosphorus over fragments of calomel (mercurous chloride) contained in a glass tube, and strongly heated. It is a thin, colourless liquid, which fumes in the air, and has a powerful and offensive odour. Its specific gravity is 1·45. Thrown into water, it sinks to the bottom, and is slowly decomposed, yielding phosphorous acid and hydrochloric acid: $PCl_3 + 3H_2O = 3HCl + H_3PO_3$.

Phosphorus Pentachloride, or **Phosphoric Chloride**, PCl_5, is formed when phosphorus is burned in excess of chlorine. Pieces of phosphorus are introduced into a large tubulated retort, which is then

filled with dry chlorine gas. The phosphorus takes fire, and burns with a pale flame, forming a white volatile crystalline sublimate, which is the pentachloride. It may be obtained in larger quantity by passing a stream of dry chlorine gas into the liquid trichloride, which becomes gradually converted into a solid crystalline mass. Phosphorus pentachloride is decomposed by water, yielding phosphoric and hydrochloric acids: $PCl_5 + 4H_2O = 5HCl + H_3PO_4$.

Phosphorus Oxychloride, $POCl_3$, is produced, together with hydrochloric acid, when phosphorus pentachloride is heated with a quantity of water insufficient to convert it into phosphoric acid. It may also be prepared by distilling the pentachloride with dehydrated oxalic acid, or by distilling a mixture of phosphorus pentachloride and phosphoric oxide. It is a colourless liquid, of sp. gr. 1·7, having a very pungent odour, boiling at 110°, readily decomposed by water into hydrochloric and phosphoric acids.

A *sulphochloride* of analogous composition is produced by the action of hydrogen sulphide on the pentachloride. It is a colourless oily liquid, decomposed by water.

Two *bromides of phosphorus*, an *oxybromide*, and a *sulphobromide*, are known, corresponding in composition and properties with the chlorine compounds, and obtained by similar processes.

Phosphorus forms also two *iodides*, PI_2 and PI_3. Both are obtained by dissolving phosphorus and iodine together in carbon bisulphide, and cooling the liquid till crystals are deposited. Whatever proportions of iodine and phosphorus may be used, these two compounds always crystallise out, mixed with excess either of iodine or of phosphorus.

The *di-iodide* melts at 110°, forming a red liquid which condenses to a light red solid. The *tri-iodide* melts at 55°, and crystallises on cooling in well-defined prisms. Both are decomposed by water, yielding hydriodic and phosphorous acids, the di-iodide also depositing yellow flakes of phosphorus.

Phosphorus and Oxygen.

There are two definite oxides of phosphorus, in which the quantities of oxygen united with the same quantity of phosphorus are to one another as 3 to 5, viz. :—

	Formula.	Composition by weight. Phosphorus.		Oxygen.
Phosphorus Trioxide, or Phosphorous oxide	P_2O_3	61·92	+	48
Phosphorus Pentoxide, or Phosphoric oxide	P_2O_5	61·92	+	80

Both these are acid oxides, uniting with water and metallic oxides to form salts, called phosphites and phosphates respect-

ively, the hydrogen salts being also called phosphorous and phosphoric acid. There are also two other oxygen-acids of phosphorus, viz., hypophosphorous acid containing a smaller proportion of oxygen than phosphorous acid, and hypophosphoric acid intermediate in composition between phosphorous and phosphoric acids.

Hypophosphorous Acid, H_3PO_2.—When phosphorus is boiled with a solution of lime or baryta, water is decomposed, giving rise to phosphine and hypophosphorous acid: the first escapes as gas, and the hypophosphorous acid remains as a barium salt:

$$P_8 + 3BaH_2O_2 + 6H_2O = 3BaH_4(PO_2)_2 + 2H_3P.$$

The soluble hypophosphite may be crystallised out by slow evaporation. On adding to the liquid the quantity of sulphuric acid necessary to precipitate the base, the hypophosphorous acid is obtained in solution, and may be reduced to a syrupy consistence by evaporation. The acid is very prone to absorb more oxygen, and is therefore a powerful deoxidising agent. All its salts are soluble in water.

Phosphorous Oxide, P_2O_3, is formed by the slow combustion of phosphorus in the air: or by burning that substance by means of a very limited supply of dry air, in which case it is anhydrous, and presents the aspect of a white powder. *Phosphorous acid*, H_3PO_3 or $3H_2O,P_2O_3$, is most conveniently prepared by adding water to the trichloride of phosphorus, when mutual decomposition takes place, the oxygen of the water being transferred to the phosphorus, generating phosphorous acid, and its hydrogen to the chlorine, giving rise to hydrochloric acid:

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3.$$

By evaporating the solution to the consistence of syrup, the hydrochloric acid is expelled, and the residue crystallises on cooling.

Phosphorous acid is very deliquescent, and very prone to attract oxygen and pass into phosphoric acid. When heated in a close vessel, it is resolved into phosphoric acid and pure phosphine gas. It is composed of 110 parts of phosphorous oxide and 54 parts of water, or 31 phosphorus, 48 oxygen, and 3 hydrogen.

Phosphoric Oxide, P_2O_5 (also called *Anhydrous Phosphoric Acid*, or *Phosphoric Anhydride*).—When phosphorus is burned under a bell-jar by the aid of a copious supply of dry air, snowlike phosphoric oxide is produced in great quantity. This substance exhibits attraction for water, stronger even than that of sulphuric oxide; in fact, sulphuric oxide may be prepared by heating strong sulphuric *acid in contact* with phosphoric oxide. Exposed to the air for a

few moments, phosphoric oxide deliquesces to a liquid, and when thrown into water, combines with the latter with explosive violence, and is converted into phosphoric acid. The water thus taken up cannot again be separated.

When nitric acid of moderate strength is heated in a retort with which a receiver is connected, and fragments of phosphorus are added singly, taking care to suffer the violence of the action to subside after each addition, the phosphorus is oxidised to its maximum, and converted into phosphoric acid. By distilling off the greater part of the nitric acid, transferring the residue in the retort to a platinum vessel, and then cautiously raising the heat to redness, the phosphoric acid may be obtained pure. This is the *glacial phosphoric acid* of the Pharmacopœia.

A third method of preparing phosphoric acid consists in taking the acid calcium phosphate produced by the action of sulphuric acid on bone-earth, precipitating it with a slight excess of ammonia carbonate, separating by a filter the insoluble calcium salt, and then evaporating and igniting in a platinum vessel the mixed phosphate and sulphate of ammonia. Phosphoric acid alone remains behind. The acid thus obtained is somewhat impure.

One of the most advantageous methods of preparing pure phosphoric acid on the large scale, is to burn phosphorus in a two-necked glass globe through which a current of dry air is passed: in this way the process may be carried on continuously. The phosphoric oxide obtained may be preserved in that state, or converted into hydrate or glacial acid, by addition of water and subsequent fusion in a platinum vessel.

Glacial phosphoric acid, or metaphosphoric acid, is exceedingly deliquescent, and requires to be kept in a closely stopped bottle. It contains 142 parts of phosphoric oxide and 18 parts of water, or 31 phosphorus, 48 oxygen, and 1 hydrogen, and is represented by the formula H_2O,P_2O_5 or HPO_3. Phosphoric oxide likewise unites with 2 and 3 molecules of water, forming the compounds $2H_2O,P_2O_5$ or $H_4P_2O_7$, and $3H_2O,P_2O_5$ or H_3PO_4, called respectively pyrophosphoric acid and orthophosphoric acid. The last is formed by oxidising phosphorus with nitric acid, and by the action of water on phosphorus pentachloride:

$$PCl_5 + 4H_2O = 5HCl + H_3PO_4.$$

The aqueous solution evaporated to a thin syrup, and left over oil of vitriol, deposits orthophosphoric acid in prismatic crystals. The same solution may be heated to 160° without change in the composition of the acid; but at 213° it gives off a molecule of water, and is converted into pyrophosphoric acid; and at a red heat it gives off another molecule of water, and leaves metaphosphoric acid. Each of these acids forms a distinct class of salts, exhibiting reactions peculiar to itself. They will be described in connection with the general theory of saline compounds.

Phosphoric oxide is readily volatilised, and may be sublimed by the heat of an ordinary spirit-lamp. The acid may be fused in a platinum crucible at a red-heat; at this temperature, it evolves considerable quantities of vapour, but is still far from its boiling point. Phosphoric acid is a very powerful acid: being less volatile than sulphuric acid, it expels the latter at higher temperatures, although it is displaced by sulphuric acid at common temperatures. Its solution has an intensely sour taste, and reddens litmus-paper; it is not poisonous.

Hypophosphoric Acid, $H_4P_2O_6 = (HO)_2OP.PO(OH)_2$. — This acid is one of the constituents of the acid liquid (Pelletier's *acide phosphatique*) formed when phosphorus partially covered with water is exposed to the air, and may be separated as a sparingly soluble sodium salt by treating that liquid with carbonate or acetate of sodium. The pure acid is best prepared by decomposing its lead salt suspended in water with hydrogen sulphide. Its aqueous solution is strongly acid, and may be boiled without decomposition, but when evaporated to a syrup it is resolved by further heating into phosphorous and phosphoric acids. It gives a white precipitate with silver salts, and is oxidised by potassium permanganate to phosphoric acid. It is quadribasic, yielding, for example, the sodium salts $Na_4(PO_3)_2$, $Na_3H(PO_3)_2$, $Na_2H_2(PO_3)_2$.

Phosphorus with Sulphur and Selenium.

Sulphides.—When ordinary phosphorus and sulphur are heated together in the dry state, or melted together under water, combination takes place, attended with vivid combustion and often with violent explosion. When amorphous phosphorus is used, the reaction is not explosive, though still very violent.

Six compounds of sulphur and phosphorus have been prepared containing the following proportions of their elements:—

	Composition by weight.		
	Phosphorus.		Sulphur.
Hemisulphide, P_4S	30·96	+	8
Monosulphide, P_2S	30·96	+	16
Sesquisulphide, P_4S_3	30·96	+	24
Trisulphide, P_2S_3	30·96	+	48
Pentasulphide, P_2S_5	30·96	+	80
Dodecasulphide, P_2S_{12}	30·96	+	192

The fourth and fifth are analogous to phosphorous and phosphoric oxides respectively; the others have no known analogues in the oxygen series. They may all be formed by heating the two bodies *together* in the required proportions; but the trisulphide and pentasulphide are more easily prepared by warming the monosulphide *with additional* proportions of sulphur. Moreover, the two lower

sulphides exhibit isomeric modifications, each being capable of existing as a colourless liquid and as a red solid.

The mono-, tri-, and penta-sulphides of phosphorus unite with metallic sulphides, forming sulphur-salts. The copper salts have the following composition:—

Hypothiophosphite,	CuS,P_2S	=	CuP_2S_2.
Thiophosphite,	CuS,P_2S_3	=	CuP_2S_4.
Thiophosphate,	CuS,P_2S_5	=	CuP_2S_6.

Selenides of Phosphorus, analogous in composition to the first, second, fourth, and fifth of the sulphides above mentioned, are produced by heating ordinary phosphorus and selenium together in the required proportions in a stream of hydrogen gas. The hemiselenide is a dark yellow, oily, fetid liquid, solidifying at 12°; the other compounds are dark red solids. The mono-, tri-, and pentaselenides unite with metallic selenides, forming selenium-salts analogous to the sulphur-salts above mentioned.

Thiophosphoric Acid, H_3PSO_3 or $PS(OH)_3$ (phosphoric acid having 1 at. O replaced by S), is not known in the free state. Its sodium salt, Na_3PSO_3, obtained by heating the corresponding chloride (*infra*) with caustic soda, forms crystals which have an alkaline reaction and are decomposed by the weakest acids, the hydrogen thiophosphate thereby produced being at once resolved into hydrogen sulphide and phosphoric acid: $PS(OH)_3 + H_2O = H_2S + PO(OH)_3$.

Thiophosphoryl Chloride, $PSCl_3$, formed by the action of phosphorus pentachloride on the pentasulphide, ($3PCl_5 + P_2S_5 = 5PSCl_3$), is a colourless, mobile, strongly refractive, pungent-smelling liquid boiling at 125°, and having a density of 1·16816 at 0°. It is decomposed by water into hydrochloric and thiophosphoric acids, the latter being then further decomposed as above.

Thiophosphoryl Bromide, $PSBr_3$, is prepared by distilling phosphorus tribromide with flowers of sulphur, or better by gradually adding bromine (8 pts.) to a well cooled solution of 1 pt. sulphur and 1 pt. phosphorus in carbon sulphide. On distilling the liquid, the carbon sulphide passes over first and then the thiobromide, which may be purified by agitation with water, whereby a hydrate, $PSBr_3,H_2O$, is formed, which gives off its water at 35°. The anhydrous compound is obtained, by evaporating its solution in carbon sulphide, as a yellow liquid, which when touched by a solid body, immediately solidifies to a crystalline mass. It is slowly decomposed by heating with water, and is partly resolved by distillation into sulphur and the compound $PSBr_3,PBr_3$ which boils at 205°.

Pyrothiophosphoryl Bromide, $P_2S_3Br_4$, is obtained by dropping *a solution of bromine* in carbon sulphide on phosphorus trisulphide.

moistened with the same liquid. It is an oily, yellow, fuming liquid, which has an aromatic pungent odour, and is resolved by heat into the ortho-compound and phosphoric sulphide: $3P_2S_3Br_4 = 4PSBr_3 + P_2S_5$.

The formation of this compound is accompanied by that of a thick yellow oily liquid—probably *metathiophosphoryl bromide*, PS_2Br, easily separated from the preceding by its insolubility in ether. Its formation is perhaps due to the reaction of the P_2S_5, formed as above, with the trisulphide and bromine, as shown by the equation, $P_2S_5 + P_2S_3 + 4Br = 4PS_2Br$.

Phosphorus and Nitrogen.

Phospham, PN_2H, formed by passing dry ammonia over PCl_5 and heating the product out of contact with the air as long as sal-ammoniac sublimes, is a light white powder insoluble in water and infusible at a red heat. When heated in the air, it slowly oxidises, giving off white fumes; and when moistened and heated it yields ammonia and metaphosphoric acid: $PN_2H + 3H_2O = 2NH_3 + PO_3H$. By fusion with caustic alkali, it is decomposed, with evolution of light and heat, yielding ammonia and an orthophosphate: $PN_2H + 3KOH + H_2O = 2NH_3 + PO(OK)_3$.

Phosphamide, $PO(NH)(NH_2)$, is obtained, together with sal-ammoniac, by the action of ammonia on phosphorus pentachloride. It is insoluble in water, and is slowly converted by boiling with water into acid ammonium phosphate: $PO(NH)(NH_2) + 3H_2O = PO(OH)(ONH_4)_2$.

Phosphoryl Triamide, $PO(NH_2)_3$, the amide of orthophosphoric acid, is obtained by the action of water on phosphorus oxychloride: $POCl_3 + 6NH_3 = 3NH_4Cl + PO(NH_2)_3$. On dissolving out the sal-ammoniac by water, the triamide remains as a white amorphous powder, not acted upon by boiling with water or aqueous potash-solution, but decomposed by sulphuric acid into phosphoric acid and ammonia: $2PO(NH_2)_3 + 3H_2SO_4 + 6H_2O = 2PO(OH)_3 + 3(NH_4)_2SO_4$. By fusion with potash it yields ammonia and potassium phosphate.

Thiophosphoryl Triamide, $PS(NH_2)_3$, is formed, together with sal-ammoniac, by the action of ammonia on phosphorus thiochloride. It is a white amorphous mass, decomposing when heated, and converted by hot water into ammonium thiophosphate, $PS(ONH_4)_3$.

Phosphoryl Nitride, PON, obtained by heating phosphamide or phosphoryl triamide out of contact with the air, is a white amorphous powder, which melts at a red heat and resolidifies to a vitreous mass. It is not attacked by nitric acid, but is converted by fusion with potash into ammonia and potassium orthophosphate: $PON + 3KOH = NH_3 + PO(OK)_3$.

Pyrophosphotriamic Acid, $P_2O_3(OH)(NH_2)_3$. This compound, derived from pyrophosphoric acid, $P_2O_3(OH)_4$, by substitution of $3NH_2$ for $3HO$, is obtained by passing ammonia into phosphorus oxychloride without cooling, and boiling the product with water: $2POCl_3 + 9NH_3 + 2H_2O = 6NH_4Cl + P_2O_3(OH)(NH_2)_3$. It is an amorphous tasteless powder, decomposed by boiling with water into ammonia and *pyrophosphodiamic acid*, $P_2O_3(OH)_2(NH_2)_2$, which is an amorphous mass soluble in water and decomposed by heat into ammonia and phosphoric oxide: $P_2O_3(OH)_2(NH_2)_2 = 2NH_3 + P_2O_5$. By continued boiling with water it is converted into pyrophosphamic acid, $P_2O_3(OH)_3NH_2$, which when similarly treated, yields ammonia phosphate and pyrophosphoric acid: $P_2O_3(OH)_3NH_2 + HOH = NH_3 + P_2O_3(OH)_4$.

Nitrogen Chlorophosphide, $P_3N_3Cl_6$, is formed by distilling the product of the action of ammonia on phosphorus pentachloride, and by distilling 1 part of the pentachloride with 2 parts sal-ammoniac. It sublimes in thin transparent six-sided plates melting at 110° and boiling at 240°. It is insoluble in water, but is slowly decomposed thereby, with formation of pyrophosphodiamic acid: $2P_3N_3Cl_6 + 15H_2O = 12HCl + 3P_2O_3(OH)_2(NH_2)_2$.

ARSENIC.

Symbol As. Atomic weight, 74·9. Vapour-density, 149·8.

Arsenic is sometimes found native: it occurs in considerable quantity as a constituent of many minerals, combined with metals, sulphur and oxygen. In the oxidised state, it has been found in very minute quantity in a great many mineral waters. The largest proportion is derived from the roasting of natural arsenides of iron, nickel, and cobalt. The operation is conducted in a reverberatory furnace, and the volatile products are condensed in a long and nearly horizontal chimney, or in a kind of tower of brickwork, divided into numerous chambers. The crude arsenious oxide thus produced is purified by sublimation, and then heated with charcoal in a retort; the arsenic is reduced, and readily sublimes.

Arsenic has a steel-grey colour, and strong lustre: it is crystalline and very brittle; it tarnishes in the air, but may be preserved unchanged in pure water. Its density, in the solid state, is 5·7 to 5·9. When heated, it volatilises without fusion, and if air be present, oxidises to arsenious oxide. Its vapour-density, compared with that of hydrogen, is 149·8, which is twice its atomic weight, so that its molecule in the gaseous state, like that of phos-

precipitate. The arsenites are, however, very unstable. Those which have the composition M_3AsO_3, or $3M_2O,As_2O_3$, are regarded as normal salts; there are also arsenites containing $M_4As_2O_5$, or $2M_2O,As_2O_3$, and $MAsO_2$, or M_2O,As_2O_3, besides acid salts. The oxide or acid has a slightly sweetish and astringent taste, and is a most fearful poison.

Arsenic Oxide, Acid and Salts.—When powdered arsenious oxide is dissolved in hot hydrochloric acid, and oxidised by the addition of nitric acid, the latter being added as long as red vapours are produced, the whole then cautiously evaporated to complete dryness, and the residue heated to low redness, arsenic oxide, As_2O_5, remains in the form of a white anhydrous mass which has no action upon litmus. When strongly heated, it is resolved into arsenious oxide and free oxygen. In water it dissolves slowly but completely, giving a highly acid solution, which, on being evaporated to a syrupy consistence, deposits, after a time, hydrated crystals of arsenic acid, containing $2H_3AsO_4,H_2O$, or $3H_2O,As_2O_5 + H_2O$. These crystals, when heated to 100°, give off their water of crystallisation and leave *trihydric arsenate*, H_3AsO_4, or $3H_2O,As_2O_5$; at 140°—160°, *dihydric arsenate*, $H_4As_2O_7$, or $2H_2O,As_2O_5$ is left; and at 260°, *monohydric arsenate*, $HAsO_3$, or H_2O,As_2O_5. The aqueous solutions of the three hydrates and of the anhydrous oxide exhibit exactly the same characters, and all contain trihydric arsenate, the other hydrates being immediately converted into that compound when dissolved in water; in this respect the hydrates of arsenic oxide differ essentially from those of phosphoric oxide (p. 231).

Arsenic acid is a very strong acid, forming salts isomorphous with the corresponding phosphates; it is also tribasic. A *sodium arsenate*, $Na_2HAsO_4,12H_2O$, undistinguishable in appearance from common sodium phosphate, may be prepared by adding the carbonate to a solution of arsenic acid, until an alkaline reaction is apparent, and then evaporating. This salt also crystallises with 7 molecules of water. Another arsenate, $Na_3AsO_4,12H_2O$, is produced when sodium carbonate in excess is fused with arsenic acid, or when the preceding salt is mixed with caustic soda. A third, NaH_2AsO_4,H_2O, is made by substituting an excess of arsenic acid for the solution of alkali. The alkaline arsenates which contain basic water lose the latter at a red heat, but, unlike the phosphates, recover it when again dissolved. The arsenates of the alkalis are soluble in water: those of the earths and other metallic oxides are insoluble, but are dissolved by acids. The reddish-brown precipitate with silver nitrate is highly characteristic of arsenic acid.

Sulphides.—Two sulphides of arsenic are known. The *disulphide*, As_2S_2, occurs native as *Realgar*. It is formed artificially by heating arsenic acid with the proper proportion of sulphur. It is an orange-red, fusible, and volatile substance, employed in painting, and by the pyrotechnist in making *white fire*. The *trisulphide* or

arsenious sulphide, As_2S_3, also occurs native as *Orpiment*, and is prepared artificially by fusing arsenic with the appropriate quantity of sulphur, or by precipitating a solution of arsenious acid with hydrogen sulphide. It is a golden-yellow, crystalline substance, fusible, and volatile by heat. A cold solution of arsenic acid is not immediately precipitated by hydrogen sulphide, but after some hours the solution, saturated with hydrogen sulphide, yields a light yellow deposit of sulphur, the arsenic acid being reduced to arsenious acid, which is then gradually converted into lemon-yellow arsenious sulphide. In boiling solutions the precipitation takes place immediately. The mixture of sulphur and trisulphide thus produced, was formerly regarded as a pentasulphide analogous to arsenic oxide.

The disulphide and trisulphide of arsenic are sulphur-acids, uniting with other metallic sulphides to form sulphur salts. Those of the disulphide are called hypothioarsenites; they are but little known. The salts of arsenious sulphide are called thioarsenites. Their composition may be represented by that of the potassium salts, viz., $KAsS_2$, or K_2S,As_2S_3; $K_4As_2S_5$, or $2K_2S,As_2S_3$; and K_3AsS_3, or $3K_2S,As_2S_3$. Of these the bibasic salts are the most common. The thioarsenites of the alkali metals and alkaline earth metals are soluble in water, and may be prepared by digesting arsenious sulphide in the solutions of the corresponding hydrates or sulphydrates; the rest are insoluble, and are obtained by precipitation. Sulphur salts, called thioarsenates, analogous in composition to the arsenates, are produced, in like manner, by digesting the mixture of sulphur and arsenious sulphide precipitated, as above mentioned, from arsenic acid, in solutions of alkaline hydrates or sulphydrates; also by passing gaseous hydrogen sulphide through solutions of arsenates. There are three thioarsenates of potassium, containing $KAsS_3$, or K_2S,As_2S_5; $K_4As_2S_7$, or $2K_2S,As_2S_5$; and K_3AsS_4, or $3K_2S,As_2S_5$. The thioarsenates of the alkali-metals and alkaline earth-metals are soluble in water; the rest are insoluble and are obtained by precipitation.

Detection of Arsenic in cases of Poisoning.

Arsenious acid is distinguished by characters which cannot be mistaken:

Silver nitrate, mixed with a solution of arsenious acid in water, occasions no precipitate, or merely a faint cloud: but if a little fixed alkali, or a drop of ammonia, be added, a yellow precipitate of silver arsenite immediately falls. This precipitate is exceedingly soluble in excess of ammonia, which must therefore be added with great caution; it is likewise very soluble in nitric acid.

Cupric sulphate gives no precipitate with solution of arsenious acid, until a little alkali has been added, when a brilliant yellow-green precipitate (Scheele's green) falls, which also is very soluble in excess of ammonia.

a U-shaped tube cooled by a freezing mixture. It may be freed from excess of chlorine by agitation with mercury and subsequent distillation. It may also be prepared by heating finely powdered boric chloride with twice its weight of phosphoric chloride for three days in a sealed tube at 150°, and subsequently distilling the product at the heat of a water-bath. It is a liquid of sp. gr. 1·35 at 17°, and boiling at 18·23°. It is decomposed by water into hydrochloric and boric acids, and fumes strongly in the air. Heated with sulphuric anhydride in a sealed tube at 120°, it yields boric oxide and sulphuryl chloride: $3SO_3 + 2BCl_3 = B_2O_3 + 3SO_2Cl_2$. It unites with ammonia, forming a white crystalline body, having the composition, $2BCl_3,3NH_3$.

Boron Bromide, BBr_3, obtained by direct combination of its elements, or by passing bromine-vapour over a heated mixture of charcoal and boric oxide, is a colourless strongly fuming liquid, having a sp. gr. of 2·69 and boiling at 90·5°. With water and with ammonia it reacts like the chloride.

Boron Fluoride, BF_3, is prepared by heating a mixture of 1 pt. boric oxide and 2 pts. fluorspar with 12 pts. strong sulphuric acid:

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O;$$

also by heating a mixture of potassium borofluoride and boric oxide with sulphuric acid:

$$6KBF_4 + B_2O_3 + 6H_2SO_4 = 8BF_3 + 6KHSO_4 + 3H_2O.$$

It is a colourless gas, having an extremely pungent odour and a density of 2·37 referred to air, or 34·25 referred to hydrogen; does not attack glass. It is decomposed by water, and must therefore be collected over mercury or by displacement.

Potassium and sodium burn brilliantly when heated in it. From certain organic bodies it withdraws the elements of water, carbonising them at the same time like strong sulphuric acid.

With an equal volume of ammonia it forms the compound BF_3NH_3, which is a white opaque solid, sublimable without alteration. With 2 or 3 vol. ammonia to 1 vol. BF_3, colourless liquids are formed having respectively the formulæ $BF_3(NH_3)_2$ and $BF_3(NH_3)_3$. These liquids when heated give off ammonia and are converted into the solid compound.

One volume of water absorbs 700 volumes of boron fluoride, with great rise of temperature and formation of a fuming oily liquid, which has a density of 1·77, and cauterises like strong sulphuric acid. When heated it gives off about a fifth of the absorbed gas, leaving a liquid which has nearly the composition BF_3,H_2O, and boils at 165°—200°, with partial decomposition and formation of boric acid.

ammonia, copper sulphate and ammonia, and hydrogen sulphide, may be applied.

When the search for solid arsenious oxide fails, the liquid itself must be examined; a tolerably limpid solution must be obtained, from which the arsenic may be precipitated by hydrogen sulphide, and the orpiment collected, and reduced to the metallic state. It is in the first part of this operation that the chief difficulty is found: such organic mixtures refuse to filter, or filter so slowly as to render some method of acceleration indispensable.* Boiling with a little caustic potash or acetic acid will sometimes effect this object. The following is an outline of a plan which has been found successful in a variety of cases in which a very small quantity of arsenious acid had been purposely added to an organic mixture: Oil of vitriol, itself perfectly free from arsenic, is mixed with the suspected liquid, in the proportion of about a measured ounce to a pint, having been previously diluted with a little water, and the whole is boiled in a flask for half an hour, or until a complete separation of solid and liquid matter becomes manifest. The acid converts any starch that may be present into dextrin and sugar: it completely coagulates albuminous substances, and casein, in the case of milk, and brings the whole in a very short time into a state in which filtration is both easy and rapid. Through the filtered solution, when cold, a current of hydrogen sulphide is passed, and the liquid is warmed, to facilitate the deposition of the arsenious sulphide, which falls in combination with a large quantity of organic matter, which often communicates to it a dirty colour. This is collected upon a small filter, and washed. It is next transferred to a capsule, and heated with a mixture of nitric and hydrochloric acids, by which the organic impurities are in great measure destroyed, and the arsenic oxidised to arsenic acid. The solution is evaporated to dryness, the soluble part taken up by dilute hydrochloric acid, and then the solution saturated with sulphurous acid, whereby the arsenic acid is reduced to a state of arsenious acid, the sulphurous acid being oxidised to sulphuric acid. The solution of arsenious acid may now be precipitated by hydrogen sulphide without any difficulty. The liquid is warmed, and the precipitate washed by decantation, and dried. It is then mixed with *black flux*, and heated in a small glass tube, similar to that already described, with similar precautions; a ring of reduced arsenic is obtained, which may be oxidised to arsenious oxide, and further examined. The black flux is a mixture of potassium carbonate and charcoal, obtained by calcining cream of tartar in a close crucible; the alkali transforms the sulphide into arsenious acid, the charcoal subsequently effecting the deoxidation. A mixture of anhydrous sodium carbonate and charcoal may be substituted with advantage for the common black flux, as it is less hygroscopic.

Other methods of proceeding, different in principle from the

* Respecting the separation of the arsenious acid by dialysis, see page 172.

foregoing, are also employed, as that of the late Mr. Marsh, which is exceedingly delicate. The suspected liquid is acidulated with sulphuric acid, and placed in contact with metallic zinc; the hydrogen reduces the arsenious acid and combines with the arsenic, if any be present. The gas is burned at a jet, and a piece of glass or porcelain held in the flame, when any admixture of arsenetted hydrogen is at once known by the production of a brilliant black metallic spot of reduced arsenic on the porcelain; or the gas is passed through a glass tube heated at one or two places to redness, whereby the arsenetted hydrogen is decomposed, a ring of metallic arsenic appearing behind the heated portion of the tube.

Antimonetted hydrogen, however, gives a similar result. In order to distinguish the two substances, the gas may be passed into a solution of silver nitrate. Both gases give rise to a black precipitate, which, in the case of antimonetted hydrogen, consists of silver antimonide, Ag_3Sb, whilst in the case of arsenetted hydrogen, it is pure silver, the arsenic being then converted into arsenious acid, which combines with a portion of silver oxide. The silver arsenite remains dissolved in the nitric acid which is liberated by the precipitation of the silver, and may be thrown down with its characteristic yellow colour by adding ammonia to the liquid filtered off from the black precipitate. The black silver antimonide, when carefully washed, and subsequently boiled with a solution of tartaric acid, yields a solution containing antimony only, from which hydrogen sulphide separates the characteristic orange-yellow precipitate of antimonious sulphide.

A convenient form of Marsh's instrument is that shown in fig. 123: it consists of a bent tube, having two bulbs blown upon it, fitted with a stop-cock and narrow jet. Slips of zinc are put into the lower bulb, which is afterwards filled with the liquid to be examined. On replacing the stop-cock, closed, the gas collects and forces the liquid into the upper bulb, which then acts by its hydrostatic pressure, and expels the gas through the jet so soon as the stop-cock is opened. It must be borne in mind that both common zinc and sulphuric acid often contain traces of arsenic. Professor Bloxam* has proposed an important modification of Marsh's process for the detection of arsenic and antimony in organic substances, which is based on the behaviour of their solutions under the influence of the electric current. Antimony is deposited in the metallic state, without any disengagement of antimonetted hydrogen, while arsenic is evolved as

Fig. 123.

* Journal of the Chemical Society, xiii. 338.

arsenetted hydrogen, which may be recognised by the characters already indicated.

A slip of copper-foil boiled in the poisoned liquid, previously acidulated with hydrochloric acid, withdraws the arsenic, and becomes covered with a white alloy. By heating the metal in a glass tube, the arsenic is expelled, and oxidised to arsenious acid. This is called Reinsch's test.

BORON.

Symbol, B. Atomic weight, 11.

THIS element is not found in nature in the free state, but occurs somewhat abundantly in the form of boric acid, $B(OH)_3$, and some of its salts.

Pure boron is prepared by heating boric oxide, B_2O_3, or potassium borofluoride, with metallic potassium in an iron tube, and washing out the soluble salts with water. As thus obtained, it is a dark brown amorphous powder destitute of taste and smell.* It burns in the air when heated, producing the trioxide, and is readily attacked by chlorine, nitric acid, fused alkalis, and other reagents.

Boron differs from all the other non-metallic elements in not combining with hydrogen; but the composition of its chloride, bromide, fluoride and oxide, show that it is trivalent; and it further resembles the other elements of the nitrogen-group in being likewise capable of functioning as a quinquivalent element, as in fluoboric acid, HBF_4, and in certain organic compounds which will be described hereafter.

HALOGEN-COMPOUNDS OF BORON.

Boron Chloride, BCl_3, is most readily obtained by passing dry chlorine over a strongly heated mixture of boric oxide and charcoal, whereupon it passes over in vapour, together with gaseous carbon monoxide, and may be condensed to a liquid by passing it through

---

* Wöhler and Deville, in 1858, by strongly igniting boric oxide with aluminium, in a crucible surrounded with powdered charcoal to prevent access of oxygen, obtained very hard transparent octohedral crystals and a graphite-like substance, which they regarded as modifications of boron analogous to the diamond and graphite varieties of carbon; but subsequent observations have shown that the octohedral crystals contained both carbon and aluminium in the proportions indicated by the formula $B_{48}C_2Al_3$, and that the graphite-like substance was a boride of aluminium having the composition AlB_2.

fied gas standing over mercury, it takes fire, and yields a deposit of amorphous silicon mixed with silica. On passing silicic hydride through a red-hot tube, it is decomposed, silicon being deposited. When passed into chlorine gas, it takes fire, forming silicon tetrachloride and hydrochloric acid.

HALOGEN-COMPOUNDS OF SILICON.

Silicon Tetrachloride, or *Silicic Chloride,* $SiCl_4$, is formed by direct combination of its elements, but is most readily prepared by mixing finely-divided silica with charcoal-powder and oil, strongly heating the mixture in a covered crucible, and then exposing the mass so obtained, in a porcelain tube heated to full redness, to the action of perfectly dry chlorine gas. A good condensing arrangement, supplied with ice-cold water, must be connected with the porcelain tube. The product is a colourless and very volatile liquid, of sp. gr. 1·524 at 0°, boiling at 50°, and having a pungent, suffocating odour. In contact with water, it yields hydrochloric acid and gelatinous silica.—*Silicon Trichloride,* Si_2Cl_6, is formed when the tetrachloride is passed over silicon, heated to whiteness in a porcelain tube. It is a colourless liquid, having a density of 1·58 at 0°, solidifying at −1°, and boiling at 146°; vapour-density, 9·7. It fumes strongly in the air, and takes fire when heated. It begins to decompose at 350°, and the decomposition goes on at an increasing rate till the temperature rises to 800°, at which point the compound is completely resolved into the tetrachloride and free silicon: $2Si_2Cl_6 = 3SiCl_4 + Si$. If, however, the temperature of the vapour be quickly raised beyond 1000°, no such decomposition takes place.

Silicon Hydrotrichloride or *Silicic Chloroform,* $SiHCl_3$ (chloroform, $CHCl_3$, having its carbon replaced by silicon), is obtained by passing dry hydrogen chloride over crystallised silicon, heated to a temperature below redness in a porcelain tube. It is a very volatile strong-smelling liquid, which fumes in the air and boils between 34° and 37°. It is very inflammable, and burns with a green-edged flame, evolving white clouds of silica. It is readily decomposed by water, with precipitation of a white powder, $Si_2H_2O_3$, called Silicoformic Anhydride, formed as shown by the equation $2SiHCl_3 + 3H_2O = 6HCl + Si_2H_2O_3$. This body is very unstable, and is decomposed by dilute ammonia, yielding silicic acid and hydrogen.

With *bromine* and *iodine,* silicon forms compounds analogous in composition to the chlorine-compounds, and prepared by similar methods:—

$SiBr_4$ is a colourless heavy liquid, boiling at 154°, and solidifying to a crystalline mass at 13°. Si_2Br_6 forms large crystalline tablets, melts when heated, and distils without decomposition at

240°. $SiCl_3Br$, prepared by heating silicochloroform with bromine at 100°, is a colourless liquid, boiling at 80°.

SiI_4, obtained by direct combination, crystallises from carbon sulphide in regular octohedrons, melts at 120·5°, and boils at 290°. It takes fire when heated in the air, burning with a reddish flame, and is decomposed by water, with formation of hydriodic and silicic acids. Si_2I_6, obtained by heating the tetra-iodide with finely-divided silver at 280°, crystallises from carbon sulphide in splendid colourless hexagonal prisms or rhombohedrons, which, on exposure to moist air, are converted into a white mass, with formation of silicic and hydriodic acids. When heated, it melts and is reduced to a lower iodide, probably Si_2I_4. Ice-cold water decomposes it, with formation of a white substance, $Si_2O_4H_2$, called *silico-oxalic acid*, from its analogy to oxalic acid, $C_2O_4H_2$. This body is decomposed, even by weak bases, into hydrogen and silica. $SiHI_3$, formed on passing a mixture of hydrogen and hydriodic acid over silicon heated to low redness, is a colourless strongly refracting liquid, having a density of 3·362 at 0°, and boiling at 220°. It is decomposed by water, like silicochloroform.

Silicon Tetrafluoride, SiF_4, is a gaseous compound, formed whenever dry hydrofluoric acid comes in contact with silica, either free or combined, and is easily prepared by heating white sand or pounded glass, with fluorspar and strong sulphuric acid :—

$$2CaF_2 + 2H_2SO_4 + SiO_2 = SiF_4 + 2CaSO_4 + 2H_2O.$$

The gas may be collected over mercury. It is colourless, and has a density of 3·57 (air = 1), or 52·2 (H = 1). It fumes strongly in the air, has a highly pungent odour, like that of hydrochloric acid, and condenses to a colourless liquid under a pressure of 30 atmospheres, or when cooled to −107°. According to Nattera, it solidifies at −140°. Fused sodium takes fire in the gas, and burns with a red flame. With dry ammonia-gas, it forms a white crystalline compound, $SiF_4,2NH_3$, which is decomposed by water.

Fig. 124.

Silicofluoric or Hydrofluosilicic Acid, H_2SiF_6 or $Si_1,2HF$, is formed, together with silicic hydroxide or silicic acid, when silicon tetrafluoride comes in contact with water : $3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$. To prepare it, silicon tetrafluoride obtained as above is passed into water through a tube, the lower end of which dips under mercury, as shown in the annexed figure ; if the gas were passed immediately into water in the ordinary way, the tube would soon be stopped up by the separated silica.

To obtain the acid, the thick jelly is pressed through a linen filter, and the filtrate is concentrated

by evaporation at a low temperature. The saturated solution is a strongly acid fuming liquid, which decomposes on boiling into silicon fluoride and hydrofluoric acid, so that it may be evaporated in platinum vessels, without leaving any residue.

Silicofluoric acid forms salts called *silicofluorides*, having the composition M_2SiF_6 or $M''SiF_6$ (M denoting a univalent and M″ a bivalent metal). Most of these are easily soluble in water, but the potassium, sodium, lithium, barium, calcium, and yttrium salts are more or less sparingly soluble. By prolonged ignition, they are resolved into silicon fluoride and a metallic fluoride: *e.g.*, $K_2SiF_6 = SiF_4 + 2KF$.

Silicon and Oxygen.

Silicon Dioxide or **Silica**, SiO_2, the only oxide of silicon, constitutes, either alone or in combination, a very large proportion of the crust of the earth. It occurs in various forms. Quartz forms crystals, sometimes very large, belonging to the hexagonal system and usually having the form of a hexagonal prism terminated by pyramidal summits. Specific gravity 2·6. The transparent colourless variety is called rock-crystal. *Amethyst quartz* has a violet tint due to traces of manganese oxides. Other varieties are known as *milk-quartz*, *rose-quartz*, and *smoky quartz*. Sand and sand-stone consist of an impure variety.—Tridymite is another hexagonal variety of silica, usually forming six-sided tables having their horizontal edges truncated by pyramidal faces; moreover the crystals usually occur in twins: hence the name. Sp. gr. 2·3.—Amorphous silica occurs as *Opal*, either colourless or variously coloured, and having a density somewhat above 2. It contains water varying in amount from 0·1 to 12·9 per cent., but this water is not regarded as essential to its constitution. *Chalcedony*, *agate*, and *flint* are intimate mixtures of amorphous silica with quartz or tridymite.

Hydrated Amorphous Silica is formed as already mentioned (p. 249) by passing silicon tetrafluoride into water. The gelatinous mass washed with water, dried, and ignited, yields pure silica in the form of a white mobile powder.

Amorphous silica may also be prepared by decomposing a silicate of alkali-metal with an acid. Powdered quartz or fine white sand is mixed with about three times its weight of dry sodium carbonate, the mixture is fused in a platinum crucible, and the glassy mass when cold is boiled with water, by which it is softened, and almost entirely dissolved. An excess of hydrochloric acid is then added to the filtered liquid, and the whole is evaporated to complete dryness. By this treatment the gelatinous silica thrown down by the acid becomes completely insoluble, and remains behind when the dry saline mass is treated with acidulated water, by which the alkaline salts, alumina, ferric oxide, lime, and many other bodies which may

happen to be present, are removed. The silica is washed, dried, and heated to redness.

Silica thus prepared is a very fine, white, tasteless powder, having a density of about 2·66, fusible only by the oxy-hydrogen blow-pipe. When once dried, it is not sensibly soluble in water or dilute acids (with the exception of hydrofluoric acid). But on adding hydrochloric acid to a very dilute solution of potassium silicate, the liberated silica remains in solution. From this mixed solution of silica and potassium chloride, the latter may be separated by diffusion (comp. p. 172), whereby a moderately concentrated solution of silica in water is obtained. This solution has a distinctly acid reaction ; it presents, however, but little stability. When kept for some time, it gelatinises, the silica separating in the insoluble modification. The same effect is produced by the addition of a few drops of sulphuric or nitric acid, or of a solution of salt.

Silica is essentially an acid oxide, forming salts with basic metallic oxides,* and decomposing all salts of volatile acids when heated with them. In strong alkaline liquids it is freely soluble. When heated with bases, especially those which are capable of undergoing fusion, it unites with them and forms salts, which are sometimes soluble in water, as in the case of the potassium and sodium silicates, when the proportion of base is considerable. Common glass is a mixture of several silicates, in which the reverse of this happens, the silica being in excess. Even glass, however, is slowly acted upon by water. Finely divided silica is highly useful in the manufacture of porcelain.

Silicon Oxychloride, Si_2Cl_6O, formed together with potassium chloride by passing the vapour of silicon tetrachloride over felspar, $Al_2K_2Si_6O_{16}$, heated to whiteness in a porcelain tube, is a colourless fuming liquid, easily decomposed by water into silicic and hydrochloric acids. By the further action of this compound on heated felspar, or better by repeatedly passing a mixture of its vapour and oxygen through a red-hot tube filled with fragments of porcelain, the following oxychlorides are produced: $Si_4Cl_4O_4$ boiling at 198—202°, $Si_3Cl_{12}O_{10}$ at about 400°, $(Si_2Cl_2O_3)_n$ above 300°, and $(Si_4Cl_2O_7)_n$ above 440°. The values of n in these last two formulæ—in other words the molecular weights of the respective compounds—are not known: those of the first two have been determined by their vapour-densities.

Silicon and Sulphur.

Silicon Disulphide, SiS_2, obtained by passing the vapour of carbon disulphide over a strongly heated mixture of silica and

* The composition of these salts will be discussed in the chapter on the general properties of the metals and their compounds.

carbon, such as is used in the preparation of silicon tetrachloride (p. 248), forms long silky needles which are decomposed by water, yielding hydrogen sulphide and silica. The *monosulphide*, SiS, and an *oxysulphide*, probably SiSO, are formed, together with other products, when sulphur-vapour is passed over white-hot silicon. The former is yellow, the latter yellowish, and both are volatile and condense in the cooler, but still hot part of the tube.

Silicon Chlorhydrosulphide, $SiCl_3SH$, is formed by passing a mixture of hydrogen sulphide and vapour of silicon tetrachloride through a red-hot tube: $SiCl_4 + H_2S = HCl + SiCl_3SH$. It is a colourless fuming liquid boiling at 96°. Vapour-density = 5·78 (air = 1).

Silicon and Nitrogen.

A *silicon nitride* of unknown composition is formed by the action of ammonia on the tetrachloride, also when crystallised silicon is strongly heated in nitrogen gas. It is a white amorphous powder insoluble in all acids except hydrofluoric acid, by which it is converted into ammonium silicofluoride. By heating with potash it is converted into ammonia and potassium silicate.

CARBON.

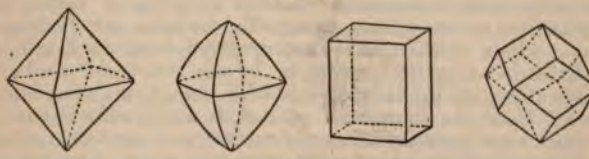
Symbol, C. Atomic weight, 12.

This element occurs in a state of purity, and crystallised, in two distinct and very dissimilar forms—namely, as diamond, and as graphite or plumbago. It constitutes a large proportion of all organic structures, animal and vegetable: when these latter are exposed to destructive distillation in close vessels, a great part of their carbon remains, obstinately retaining some of the hydrogen and oxygen, and associated with the earthy and alkaline matter of the tissue, giving rise to the many varieties of charcoal, coke, &c. This residue, when perfectly separated from foreign matter, constitutes a third variety of carbon.

The diamond is one of the most remarkable substances known: long prized on account of its brilliancy as an ornamental gem, the discovery of its curious chemical nature confers upon it a high degree of scientific interest. Several localities in India, the Island of Borneo, South Africa, and Brazil, furnish this beautiful substance. It is always distinctly crystallised, often quite transparent and colourless, but now and then having a shade of yellow, pink, or blue. The origin and true geological position of the diamond are unknown; it is always found imbedded in gravel and transported materials whose history cannot be traced. The crystalline form of

the diamond is that of the regular octohedron or cube, or some figure geometrically connected with these. Many of the octohedral crystals exhibit a very peculiar appearance, arising from the faces being curved or rounded, which gives to the crystal an almost spherical figure.

Fig. 125.



The diamond is the hardest substance known : it admits of being split or cloven without difficulty in particular directions, but can only be cut or abraded by a second portion of the same material ; the powder rubbed off in this process serves for polishing the new faces, and is also highly useful to the lapidary and seal-engraver. One very curious and useful application of the diamond is made by the glazier ; a *fragment* of this mineral, like a bit of flint, or any other hard substance, scratches the surface of the glass ; a *crystal* of diamond, having the rounded octohedral figure spoken of, held in one particular position on the glass—namely, with an edge formed by the meeting of two adjacent faces—presented to the surface and then drawn along with gentle pressure, causes a split or cut, which penetrates to a considerable depth into the glass, and determines its fracture with perfect certainty.

The diamond is infusible and unalterable even by a very intense heat, provided air be excluded ; but when heated, thus protected, between the poles of a strong galvanic battery, it is converted into coke or graphite ; heated to whiteness in a vessel of oxygen, it burns with facility, yielding carbonic acid gas.

Graphite or plumbago appears to consist essentially of pure carbon, although most specimens contain iron, the quantity of which varies from a mere trace up to 5 per cent. Graphite is a somewhat rare mineral ; the finest and most valuable for pencils was formerly obtained from Borrowdale, in Cumberland, where a kind of irregular vein is found traversing the ancient slate beds of that district, but the mine is now nearly exhausted. Large quantities of graphite are imported from Germany, the East Indies, and the United States.* Crystals are not common ; when they occur,

* The graphite which can be directly cut for pencils, occurring only in limited quantity, powdered graphite, obtained from the inferior varieties of the mineral, is now frequently consolidated for this purpose. The mechanical division of graphite presents considerable difficulties

ing a light. It is easily distinguished from nitrogen, which is also incapable of supporting combustion, by its rapid absorption by caustic alkali, or by lime-water; the turbidity communicated to the latter from the production of insoluble calcium carbonate is very characteristic.

Cold water dissolves about its own volume of carbon dioxide, whatever be the density of the gas with which it is in contact (comp. p. 174); the solution temporarily reddens litmus-paper. Common soda-water and effervescent wines afford examples of the solubility of the gas. Even boiling water absorbs a perceptible quantity.

Some of the interesting phenomena attending the liquefaction of carbon dioxide have been already described (p. 62): it requires for the purpose a pressure of 38·5 atmospheres at 0°. The liquefied oxide is colourless and limpid, lighter than water, and four times more expansible than air; it mixes in all proportions with ether, alcohol, naphtha, oil of turpentine, and carbon disulphide, and is insoluble in water and fat oils. In this condition it does not exhibit any of the properties of an acid.

Carbon dioxide exists, as already mentioned, in the air: relatively its quantity is but small; but absolutely, taking into account the vast extent of the atmosphere, it is very great, and fully adequate to the purpose of supplying plants with their carbon, these latter having the power, by the aid of their green leaves, of decomposing carbon dioxide, retaining the carbon, and expelling the oxygen. The presence of light is essential to this effect, but the manner of its production is not yet clearly understood.

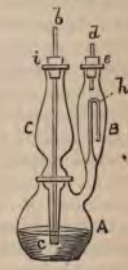
The carbonates form a very large and important group of salts, some of which, as the carbonates of calcium and magnesium, occur very abundantly in nature. They contain the elements of carbon dioxide and a metallic oxide: calcium carbonate, for example, being represented by the formula CaO,CO_2 or $CaCO_3$; but they are never formed by the direct union of dry carbon dioxide with a dry metallic oxide, the intervention of water being always required to bring about the combination. Potassium carbonate (pearlash) is the chief constituent of wood-ashes: sodium carbonate is contained in the ashes of marine plants, and is manufactured on a very large scale by heating sodium sulphate with lime and coal. These carbonates are soluble in water. The other metallic carbonates, which are insoluble, may be formed by mixing a solution of potassium or sodium carbonate with a soluble metallic salt; thus, when solutions of lead nitrate and sodium carbonate are mixed together, the lead and sodium change places, forming sodium nitrate, which remains dissolved, and lead carbonate, which, being insoluble in water, is precipitated as a white powder: $Pb(NO_3)_2 + Na_2CO_3 = 2NaNO_3 + PbCO_3$.

The solution of carbon dioxide in water may be supposed to contain hydrogen carbonate or carbonic acid, H_2CO_3 or H_2O,CO_2; but this compound is not known in the separate state, only in

aqueous solution. According to Wroblewski,* however, carbon dioxide unites with water at 0° C. and under a pressure of about 16 atmospheres, forming the hydrate $CO_2,8H_2O$.

The amount of carbon dioxide contained in a carbonate may be estimated by the loss of weight which the salt undergoes when decomposed by an acid. This may be determined by means of Geissler's apparatus (fig. 127). It consists of three glass vessels, A, B, C, the last of which is ground air-tight into the neck of A; *b c* is a glass tube open at both ends, ground water-tight into C at the lower end, and kept in position by the cork *i*, which can slide up and down on the tube *b c*. The cork *e* must close air-tight in B, and the tube *d* in *e*. The weighed substance to be decomposed is introduced into A, and water is added. The vessel C is then filled with the aid of a pipette nearly to the top with dilute nitric or hydrochloric acid, the cork *i* having been previously moved upwards without raising the tube *b*. The cork *i* is then replaced; the vessel C again inserted into A; the vessel B is rather more than half filled with strong sulphuric acid; and the tube *b* is closed at the top by placing over it a small piece of caoutchouc tubing, with a glass rod fitted into the other end. The apparatus having been weighed, the decomposition of the carbonate is effected by opening the tube *b* a little, so as to cause acid to pass from C into A. The carbon dioxide then passes through the bent tube *h* into the sulphuric acid, by which it is dried, and finally leaves the apparatus through *d*. When the decomposition is complete, the vessel A is gently heated, the stopper is removed from *b*, and the carbon dioxide still remaining in the apparatus is sucked out at *d*. The apparatus, after cooling, is again weighed, and the difference between the two weighings gives the weight of the carbon dioxide expelled.

Fig. 127.



Carbon and Sulphur.

Two compounds of these elements are known, viz., the disulphide produced by the direct combination of its elements at a high temperature, and the monosulphide formed by reduction of the disulphide.

Carbon Disulphide or **Bisulphide**, CS_2.—To prepare this compound, a wide porcelain tube filled with pieces of charcoal which have been previously heated to redness in a covered crucible, is fixed across a furnace in a slightly inclined position. Into the lower extremity a tolerably wide tube is secured by a cork; this tube bends downwards, and passes nearly to the bottom of a bottle filled

* Comptes rendus, xciv. 954.

mixture burning with a shining bluish-white flame. It is not acted upon by chlorine or fuming nitric acid at ordinary temperatures, and does not form an explosive mixture with nitrogen dioxide.

Water absorbs about its own volume of carbon oxysulphide, acquiring a sweetish and afterwards a pungent taste, and decomposing it after some time. It appears to exist in some sulphur springs and in the sulphurous gases of volcanos. Potash-solution absorbs the gas as completely as carbon dioxide, though less quickly; the solution exhibits the reactions of metallic sulphides, and when treated with acids gives off hydrogen sulphide and carbon dioxide. Baryta-water and lime-water act in a similar manner. Neutral or acid solutions of lead, copper, cadmium, and silver salts are not precipitated by the gas, but when mixed with excess of ammonia they yield with it characteristic precipitates of metallic sulphides.*

Compound of Carbon and Nitrogen. Cyanogen, CN.

When a stream of air is passed over a mixture of charcoal and potassium carbonate kept at a bright red heat, the nitrogen of the air unites with the carbon and the potassium, forming a compound called potassium cyanide, containing 39 parts of potassium, 12 of carbon, and 14 of nitrogen, and represented by the formula KCN. It is a crystalline salt, which dissolves easily in water, and decomposes mercuric oxide, forming potassium hydrate and mercuric cyanide:

$$2KCN + H_2O + HgO = 2KHO + HgC_2N_2.$$

Now, when dry mercuric cyanide, which is a white crystalline substance, is strongly heated in a glass tube, fitted up like that used for the evolution of oxygen from mercuric oxide (p. 29) it splits up, like the oxide, into metallic mercury, and a gaseous body called cyanogen, containing 12 parts by weight of carbon and 14 of nitrogen, and represented by the formula CN. It must be collected over mercury, as it is rapidly absorbed by water.

Cyanogen is a colourless gas, having a pungent and a very peculiar odour, remotely resembling that of peach-kernels. Exposed while at the temperature of 45° F (7·2° C.) to a pressure of 3·6 atmospheres, it condenses to a thin, colourless, transparent liquid. It is inflammable, and burns with a beautiful purple or peach-blossom-coloured flame, generating carbon dioxide and liberating nitrogen. Its specific gravity is 1·801 referred to air, or 26 referred to hydrogen as unity. One volume of it exploded with 2 vols. oxygen, yields 1 vol. nitrogen and 2 vols. carbon dioxide. Now, the weights of equal volumes of cyanogen, nitrogen, and carbon dioxide are as 26 : 14 : 22. Consequently, 26 parts by weight of cyanogen yield

* See further, Watts's Dictionary of Chemistry, First Supplement, 406; Second Supplement, p. 262.

by combustion 14 parts of nitrogen and 44 parts of carbon dioxide, containing 12 parts of carbon; or 26 cyanogen = 12 carbon + 14 nitrogen.

Water dissolves 4 or 5 times its volume of cyanogen gas, and alcohol a much larger quantity: the solution rapidly decomposes, yielding ammonium oxalate, a brown insoluble matter, and other products.

Cyanogen unites (though not directly) with hydrogen, forming the very poisonous compound called hydrocyanic or prussic acid; and with metals, forming compounds called cyanides, analogous in composition and character to the chlorides, iodides, bromides, &c. In short, this group of elements, represented by the formula CN, combines with elementary bodies, and is capable of passing from one state of combination to another, just as if it were itself an elementary body. Such a group of elements is called a compound radicle. We have already had occasion to notice another such group, viz., ammonium, NH_4. Cyanogen, however, is analogous in its chemical relations to the non-metallic elements, chlorine, bromine, oxygen, &c., whereas ammonium is a quasi-metal analogous to potassium, &c.

The compounds of cyanogen will be further considered under ORGANIC CHEMISTRY.

Compounds containing Carbon and Silicon.

When crystallised silicon is heated nearly to whiteness in a porcelain tube through which a stream of carbon dioxide is passing, a greenish-white mass is formed, which when freed from silica by hydrofluoric acid, leaves a greenish powder having the composition SiCO, and formed according to the equation $3Si + 2CO_2 = SiO_2 + 2SiCO$. It is oxidised, with incandescence, when heated with litharge or a mixture of litharge and lead chromate.

When crystallised silicon is heated to whiteness in a crucible lined with charcoal, the mass, after washing with boiling potash and with hydrofluoric acid, yields a bluish-green pulverulent residue, Si_2C_2N, which is insoluble in acids and in alkalis, and burns brilliantly, with formation of Cl_2 and nitrogen oxides, when heated with lead oxide or a mixture of lead oxide and chromate.*

When hydrogen gas saturated with benzene vapour at 50—60° is passed over silicon contained in two porcelain dishes heated to bright redness in a porcelain tube, the first dish, after a few hours, is found to contain a light black powder, and the second a grey substance, both of which may be purified by treatment with potash and hydrofluoric acid. The black powder then consists of uncombined carbon mixed with the dark green compound SiC_2, which does not burn in a stream of oxygen. The grey substance is somewhat variable in

* Schützenberger and Colson, Comptes rendus, xcii. 1508.

The weights of the three atoms concerned in this reaction are to one another in the same proportion as the equivalent weights, or, taking the hydrogen as the unit in each case, we may say that the atomic weights of sodium and chlorine are identical with their equivalent weights.

(2.) Each molecule of water must be supposed to contain two atoms of hydrogen: for if it contained only one atom, then since the first action of the sodium is to expel only half the hydrogen, it would follow that each atom of hydrogen would be split into two, and that each molecule of sodium hydroxide would contain only half an atom of hydrogen; this, however, is at variance with the fundamental notion of atoms, namely, that they are indivisible. These two atoms of hydrogen are combined with a quantity of oxygen weighing 16, which is therefore the smallest quantity of oxygen capable of entering into the reaction under consideration:

H	H	O	+	Na	=	H	Na	O	+	H
1	1	16		23		1	23	16		1

and we shall hereafter find that the same is true with regard to all other well-defined reactions in which oxygen takes part. Hence this quantity of oxygen, 16 parts by weight (hydrogen being the unit), is regarded as the weight of the atom of oxygen.

This atomic weight of oxygen is not equal to the equivalent weight, as in the case of chlorine, but *twice as great*, 8 parts of oxygen being the quantity which is capable of replacing 1 part of hydrogen in combination, and may in many cases be directly substituted for it, as when alcohol, a compound of 12 parts carbon, 3 hydrogen, and 8 oxygen, is oxidised to acetic acid containing 12 carbon, 2 hydrogen, and 16 oxygen.

Let us now consider the hydrogen-compound of nitrogen, that is to say, *ammonia*. This is composed of 1 part of hydrogen united with $4\frac{2}{3}$ or $\frac{14}{3}$ of nitrogen, or 3 parts hydrogen with 14 parts nitrogen. Now in this compound the hydrogen is replaceable by thirds. When potassium is heated in ammonia gas, a compound called potassamine is formed, in which one-third of the hydrogen is replaced by potassium. Another compound, called tripotassamine, is also known, consisting of ammonia in which the whole of the hydrogen is replaced by an equivalent quantity of potassium.

There is also a large class of compounds derived from ammonia in like manner by the replacement of $\frac{1}{3}$, $\frac{2}{3}$, or the whole of the hydrogen by equivalent quantities of certain groups of elements called *compound radicles* (see page 288). Hence, by reasoning similar to that which was above applied to water, it is inferred that the molecule of ammonia contains 3 atoms of hydrogen, and that the atomic weight of nitrogen is 14. Moreover, in certain organic compounds this quantity of nitrogen may be substituted for 3 parts of hydrogen, or $\frac{14}{3}$ nitrogen for 1 hydrogen; consequently the atomic weight of nitrogen is *three* times its equivalent weight.

Next take the case of *marsh gas* or *methane*, a compound of 1 part hydrogen with 3 parts carbon, or 4 of hydrogen with 12 of carbon. When this gas is mixed with chlorine, and exposed to diffuse daylight, a new compound is formed, in which one-fourth of the hydrogen belonging to the marsh gas is replaced by an equivalent quantity of chlorine; and if the chlorine is in excess, and the mixture exposed to sunshine, three other compounds are formed, in which one-half, three-fourths, and all the hydrogen are thus replaced. The results may be thus expressed:—

Methane.

Carbon.		Hydrogen.				
12	+	1	+ 1	+ 1	+ 1	

Chloromethane.

Carbon.		Hydrogen.				Chlorine.
12	+	1	+ 1	+ 1	+	35·4

Dichloromethane.

Carbon.		Hydrogen.		Chlorine.		
12	+	1	+ 1	+ 35·4	+	35·4

Trichloromethane or Chloroform.

Carb.		Hyd.	Chlorine.		
12	+	1	+ 35·4	+ 35·4	+ 35·4

Tetrachloromethane.

Carbon.		Chlorine.			
12	+	35·4	+ 35·4	+ 35·4	+ 35·4

Hence, by reasoning similar to the above, it is inferred that the molecule of methane contains 4 atoms of hydrogen, and that the atomic weight of carbon is 12. Moreover, as this quantity of carbon can unite with 4 × 35·4 parts, or 4 atoms of chlorine, it follows that the atomic weight of carbon is equal to four times its equivalent weight.

We have thus shown in three cases how the atomic weight of an element may be determined by the proportion in which equivalent substitution takes place in its compounds with hydrogen. Sulphur, selenium, and tellurium form hydrogen-compounds exactly analogous in this respect to water, the hydrogen being replaceable by halves; their atomic weights are therefore double of their equivalent weights. Silicon forms with chlorine a compound containing 7 parts silicon with 35·4 parts chlorine; and in this one-fourth of

the chlorine is replaceable by hydrogen or by bromine: hence the atomic weight of silicon is, like that of carbon, equal to four times the equivalent weight, its numerical value being 28. There are also some elements in which the atomic weight is equal to five times, others in which it is equal to six times, and others in which it is perhaps equal to seven times or eight times the equivalent weight: higher ratios have not been observed.

It must not be supposed that the atomic weights of elementary bodies are always actually determined in the manner above described. There are several other methods of determining their numerical values, as will be presently explained, and the values obtained by different methods do not always exhibit exact agreement; but the atomic weights of all the more important elements may be regarded as definitely fixed within very small numerical errors. The equivalent value of an element, or the ratio of the equivalent to the atomic weight, is also subject to some variation, as will be presently explained, according to the view which may be taken of the constitution of particular compounds.

The values of the atomic weights on which chemists are now, for the most part, agreed, are given in the table on page 3.

Physical and Chemical Relations of Atomic Weights.

The atomic weights of the elementary bodies exhibit some remarkable relations to their physical properties, and to the proportions in which they unite by volume.

1. **To the Specific Heats of the Elementary Bodies.**—Dulong and Petit, in the course of their investigations on specific heat, observed that if the specific heats of bodies be computed upon equal weights, numbers are obtained all different, and exhibiting no simple relations amongst themselves; but if, instead of equal weights, quantities be taken in the proportion of the atomic weights, the resulting specific heats come out very nearly equal, at least in the case of solid and liquid elements, showing that some very intimate connection must exist between the relation of bodies to heat, and their chemical nature.

In the following table the solid and liquid elementary bodies are arranged in the order of their specific heats, as determined by Regnault, beginning with those whose specific heat is the greatest; and this order, it will be observed, is the inverse of that of the atomic weights in the third column:—

Specific Heats of Elementary Bodies.

Elements.	Specific heat (that of water = 1).	Atomic weights.	Product of sp. heat × at. weight.
Lithium	0·9408	7	6·59
Sodium	0·2934	23	6·75
Aluminium	0·2143	27·3	5·85
Phosphorus liquid	0·2120	31	6·57
Phosphorus solid	0·1887	31	5·85
Sulphur	0·2026	32	6·48
Potassium	0·1660	39	6·48
Iron	0·1138	55·9	6·36
Nickel	0·1080	58·6	6·33
Cobalt	0·1070	58·6	6·27
Copper	0·0952	63·0	6·00
Zinc	0·0956	64·9	6·20
Arsenic	0·0822	74·9	6·16
Selenium	0·0762	79	6·02
Bromine (solid)	0·0843	79·75	6·72
Palladium	0·0593	106·2	6·30
Silver	0·0570	107·7	6·13
Cadmium	0·0567	111·6	6·33
Indium	0·0570	113·4	6·46
Tin	0·0548	117·8	6·46
Antimony	0·0523	122	6·38
Iodine	0·0541	126·5	6·84
Tellurium	0·0475	128	6·08
Gold	0·0324	196·2	6·36
Platinum	0·0324	196·7	6·37
Mercury (solid)	0·0319	199·8	6·37
Thallium	0·0335	203·6	6·82
Lead	0·0314	206·4	6·50
Bismuth	0·0308	210	6·48

A comparison of the numbers in the fourth column of this table shows that, for a considerable number of elementary bodies in the solid state, the specific heats are very nearly proportional to the atomic weights, so that the products of the specific heats of the elements into their atomic weights give nearly a constant quantity, the mean value being 6·4. This quantity may be taken to represent the *atomic heat* of the several elements in the solid state, or the quantity of heat which must be imparted to or removed from atomic proportions of the several elements, in order to produce equal variations of temperature.

Carbon, boron, and silicon were formerly regarded as exceptions to this law, their atomic heats, calculated from the specific heats

determined at ordinary temperatures, being considerably below the mean value of those of the other elements, as shown by the following table:—

Elements.		Specific heat.	Atomic weights.	Product of sp. heat × at. weight.
Boron		0·2500	11	2·75
Carbon	wood charcoal	0·2415	12	2·90
	graphite	0·2008		2·41
	diamond	0·1469		1·76
Silicon	crystallised	0·1774	28	4·97
	fused	0·1750		4·70

F. Weber has, however, lately shown* that the specific heats of these three bodies increase rapidly at higher temperatures, and that at particular temperatures (about 600° for carbon) they become constant, giving for the atomic heats a mean value of about 6, which is nearly the same as that of other elements of small atomic weight, like aluminium and phosphorus, thus:—

	Sp. Heat.	At. Weight.	At. Heat.
Silicon	0·203	28	5·7
Carbon	0·467	12	5·6
Boron	0·5	11	5·5

The specific heats and molecular weights of similarly constituted compounds exhibit, for the most part, the same relation as that which is observed between the specific heats and atomic weights of the elements.

2. **To the Crystalline Forms of Compounds.**—It is found that in many cases two or more compounds which, from chemical considerations, are supposed to contain equal numbers of atoms of their respective elements, crystallise in the same or in very similar forms. Such compounds are said to be *isomorphous*.† Thus the sulphates constituted like magnesium sulphate, $MgSO_4 + 7H_2O$, are isomorphous with the corresponding selenates, *e.g.*, $MgSeO_4 + 7H_2O$.

Accordingly these isomorphous relations are often appealed to for the purpose of fixing the constitution of compounds, and thence deducing the atomic weights of their elements, in cases which would otherwise be doubtful. Thus aluminium forms only one oxide, viz.,

* Ann. Chim. Phys. [5], viii. 132.

† Ἴσος, equal; μορφή, form.

alumina, which is composed of 18·3 parts by weight of aluminium and 16 parts of oxygen. What, then, is the atomic weight of aluminium? The answer to this question will depend upon the constitution assigned to alumina, whether it is a monoxide, sesquioxide, dioxide, &c. Thus:—

			O.		Al.
Monoxide .	AlO	=	16	+	18·3
Sesquioxide	Al_2O_3	=	48	+	27·4 27·4
Dioxide .	AlO_2	=	32	+	36·6
Trioxide .	AlO_3	=	48	+	54·8

The numbers in the last column of this table are the weights which must be assigned to the atom of aluminium, according to the several modes of constitution indicated in the first column; but there is nothing in the constitution of the oxide itself that can enable us to decide between them. Now iron forms two oxides, in which the quantities of oxygen united with the same quantity of iron are to one another as 1 : $1\frac{1}{2}$, or as 2 : 3. These are therefore regarded as monoxide, FeO, and sesquioxide, Fe_2O_3, and this last oxide is known to be isomorphous with alumina. Consequently alumina is also regarded as a sesquioxide, Al_2O_3, and the atomic weight of aluminium is inferred to be 27·4.

3. To the Volume-relations of Elements and Compounds.—The atomic weights of those elements which are known to exist in the state of gas or vapour are, with one or two exceptions, proportional to their specific gravities in the same state. Taking the specific gravity of hydrogen as unity, those of the following gases and vapours are expressed by numbers identical with their atomic weights:—

Hydrogen . . .	1	Oxygen	16
Chlorine . . .	35·4	Sulphur	32
Bromine . . .	80	Selenium . . .	79
Iodine	127	Tellurium . . .	128

The exceptions to this rule are exhibited by *phosphorus* and *arsenic*, whose vapour-densities are twice as great as their atomic weights, that of phosphorus being 62, and that of arsenic 150; and by *mercury* and *cadmium*, whose vapour-densities are the halves of their atomic weights, that of mercury being 100, and that of cadmium 56.

From these relations, considered in connection with above explained laws of combination by weight, it follows that the volumes of any two elementary gases which make up a compound molecule, are to one another in the same ratio as the numbers of atoms of the same elements which enter into the compound, excepting in the case of phosphorus and arsenic, for which the number of volumes thus

determined has to be halved, and of mercury and cadmium, for which it must be doubled: thus—

The molecule	HCl	contains	1	vol.	H	and 1	vol.	Cl
„	H_2O	„	2	„	H	„ 1	„	O
„	H_3N	„	3	„	H	„ 1	„	N
„	H_3P	„	3	„	H	„ ½	„	P
			or 6	„	H	„ 1	„	P
„	Cl_3As	„	3	„	Cl	„ ½	„	As
			or 6	„	Cl	„ 1	„	As
„	Cl_2Hg	„	2	„	Cl	„ 2	„	Hg

If the smallest volume of a gaseous element that can enter into combination be called the combining volume of that element, the law of combination may be expressed as follows:—*The combining volumes of all elementary gases are equal, excepting those of phosphorus and arsenic, which are only half those of the other elements in the gaseous state, and those of mercury and cadmium, which are double those of the other elements.*

It appears, then, that in all cases the volumes in which gaseous elements combine together may be expressed by very simple numbers. This is the "Law of Volumes," first observed by Humboldt and Gay-Lussac in 1805, with regard to the combination of oxygen and hydrogen, and afterwards established in other cases by Gay-Lussac, whose observations, published in his "Theory of Volumes," afforded new and independent evidence of the combination of bodies in definite and multiple proportions, in corroboration of that derived from the previously observed proportions of combination by weight.

Gay-Lussac likewise observed that the product of the union of two gases, when itself a gas, sometimes retains the original volume of its constituents, no contraction or change of volume resulting from the combination, but that when contraction takes place, which is the most common case, the volume of the compound gas always bears a simple ratio to the volumes of its elements: and subsequent observation, extended over a very large number of compounds, organic as well as inorganic, has shown that, with a few exceptions, probably only apparent, *the molecules of compound bodies in the gaseous state occupy twice the volume of an atom of hydrogen gas.* No matter what may be the number of atoms or volumes that enter into the compound, they all become condensed into two volumes; thus—

1	vol. H	and 1	vol. Cl	form	2	vol.	HCl,	hydrochloric acid.
1	„ N	„ 1	„ O	„	2	„	NO,	nitrogen dioxide.
2	„ H	„ 1	„ O	„	2	„	H_2O,	water.
3	„ H	„ 1	„ N	„	2	„	H_3N,	ammonia.
2	„ H	„ ½	„ P	„	2	„	H_3P,	hydrogen phosphide.

Similarly in the union of compound gases, *e.g.*,

1 vol. ethyl, C_2H_5, and 1 vol. Cl form 2 vol. C_2H_5Cl, ethyl chloride.
2 „ ethyl, C_2H_5, „ 1 „ O „ 2 „ $(C_2H_5)_2O$, ethyl oxide.
2 „ ethylene, C_2H_4, „ 2 „ Cl „ 2 „ $C_2H_4Cl_2$, ethylene chloride.
2 „ ethylene, C_2H_4, „ 1 „ O „ 2 „ C_2H_4O, ethylene oxide.

It will presently be shown, as at least highly probable, that the molecule of an elementary gas in the free state is made up of two atoms, HH for example. The law just enunciated may therefore be generalised as follows. *The molecules of all gases, simple or compound, occupy equal volumes;* or, *equal volumes of all gases contain equal numbers of molecules.*

This is called the "Law of Avogadro," having been first enunciated (in 1811) by an Italian physicist of that name. It is quite in accordance with the observed fact that all perfect gases, simple and compound, are equally affected by equal variations of pressure and temperature; and indeed it may be shown, by mathematical reasoning, to follow as a necessary consequence from the physical constitution of gases as explained in connection with the dynamical theory of heat (pp. 77–81); but the demonstration is not of a nature adapted for an elementary book. The law may, however, be considered as completely established by the relations between the combining proportions of the elements by weight and by volume as already explained, and it is now regarded as affording the surest method of fixing the molecular constitution of all compounds that can be obtained in the gaseous state, and the atomic weights of the elements contained in them.

Suppose, for example, it were required to determine the atomic weight of tin. This metal forms a volatile chloride (stannic chloride), in which 29·45 parts of tin are combined with 35·4 of chlorine. 29·45 is therefore the equivalent of tin in this compound. Now the vapour-density of this chloride referred to hydrogen as unity, is 129·7: consequently the weight of two volumes of its vapour is 259·4, and this contains 4 × 35·4, or 141·6 parts of chlorine and 117·8 parts of tin; and as this appears to be the chloride containing the largest proportion of chlorine or the smallest proportion of tin, it is regarded as a compound of 4 atoms of chlorine and 1 atom of tin, and the atomic weight of tin is thus found to be 117·8.

When an element does not form any volatile compounds whose vapour-densities can be exactly ascertained, its atomic weight may be determined by its specific heat, according to the law of Dulong and Petit (p. 272), or by its isomorphous relations with other elements, as already explained in the case of aluminium. To give an instance of the determination of the atomic weight of an element according to its specific heat, we may take the case of indium. This metal forms a chloride containing 35·4 parts of chlorine and 37·8 parts of indium, which latter number is therefore the equivalent weight of the metal. Now when indium was first discovered (in 1863), this chloride was, for reasons which need not here be specified, regarded as a dichloride, $InCl_2$, and consequently the atomic weight

of indium was supposed to be 75·6. Subsequently, however, Bunsen showed that the specific heat of indium, referred to the unit of weight, is 0·057, and this number multiplied by 75·6 gives for the atomic heat the number 4·5, which does not agree with the law of Dulong and Petit; but if the chloride be regarded as a trichloride, MCl_3, making the atomic weight of the metal equal to three times its equivalent weight, or 113·4, the atomic heat becomes 6·15, which agrees very nearly with the general law. This number 113·4 is therefore now adopted as the atomic weight of indium.

Specific or Atomic Volume.

These terms denote the quotient obtained by dividing the molecular weight of a body by its specific gravity. Now from the law of condensation in the combination of gases above detailed (p. 277) it follows that *the specific gravity of any compound gas or vapour referred to hydrogen as unity, is equal to half its atomic or molecular weight:* hence also, *the specific volumes of compound gases or vapours referred to that of hydrogen as unity are, with a few exceptions, equal to* 2. It will presently be shown that the same law applies to the specific volumes of the elementary gases themselves.

Some compounds, however, exhibit a departure from this rule, their observed specific gravities being equal to only one-fourth their molecular weights, or their molecules occupying four times the volume of an atom of hydrogen. Such is the case with sal-ammoniac, NH_4Cl, phosphorus pentachloride, PCl_5, sulphuric acid, H_2SO_4, ammonium hydrosulphide, $(NH_4)SH$, and a few others. This anomaly is probably due, in some cases at least, to a decomposition or "dissociation" of the compound at the high temperature to which it is subjected for the determination of its vapour-density; NH_4Cl, for example, splitting up into NH_3 and HCl, each of which occupies two volumes, and the whole therefore four volumes; and in like manner H_2SO_4 may be supposed to separate into H_2O and SO_3; PCl_5 into PCl_3 and Cl_2; $(NH_4)SH$ into NH_3 and H_2S, &c.

On the other hand, some substances, both simple and compound, exhibit, at temperatures not far above their boiling points, vapour-densities considerably greater than they should have according to the general law, whereas when raised to higher temperatures they exhibit normal vapour-densities. Thus sulphur, which boils at 440°, exhibits at 1000°, like elementary gases in general, a vapour-density equal to its atomic weight, viz., 32; but at 500° its vapour-density is nearly three times as great. Again, acetic acid, $C_2H_4O_2$, whose molecular weight is $24 + 4 + 16 = 60$, has, at temperatures considerably above its boiling point, a vapour-density nearly equal to 30; but at 125° (8 degrees above its boiling point), its vapour-density is rather more than 45, or $1\frac{1}{2}$ times as great. This anomalous increase of vapour-density appears to take place when the substance approaches its liquefying point, at which also it exhibits

irregularities in its rate of expansion and contraction by variations of pressure and temperature—at which, in short, it begins to behave itself like a liquid; but at higher temperatures it exhibits the physical characters of a perfect gas, and then also its specific gravity becomes normal.

Specific Volumes of Liquids and Solids.—The following table exhibits the specific volumes of those solid and liquid elements whose specific gravities have been determined with sufficient accuracy. The elements are arranged in the order of their specific volumes, beginning with the smallest.

Specific Volumes of Solid and Liquid Elements.

	Atomic weight.	Specific gravity.	Specific volume.		Atomic weight.	Specific gravity.	Specific volume.
Carbon, as *diamond*	12	3·52	3·4	Mercury, *liquid*	199·8	14·8	13·5
Beryllium	9·0	2·1	4·4	Sulphur, *trimetric*	32	2·07	15·2
Carbon, as *graphite*	12	2·3	5·2	Indium	113·4	7·4	15·3
Nickel	58·6	8·6	6·8	Phosphorus, *red*	31	1·94	15·8
Manganese	55	8·03	6·85	Sulphur, *monoclinic*	32	1·98	16·2
Cobalt	58·6	8·50	7·0	Tin	117·8	7·3	16
Iron	56	7·8	7·2	Selenium, *granular*	79·0	4·80	16·4
Copper	63·4	8·95	7·2	Phosphorus, *yellow*	31	1·84	16·8
Chromium	52·4	7·01	7·4	Antimony	122	6·7	18·2
Iridium	196·7	21·8	9·1	Lead	206·4	11·33	18
Platinum	196·7	21·5	9·2	Selenium, *amorphous*	79·4	4·28	18·1
Zinc	64·9	7·1	9·1	Tellurium	128	6·2	20·6
Palladium	106·2	11·8	9·2	Bismuth	210	9·8	21·2
Rhodium	104·1	11·0	9·4	Sodium	23	0·97	23·7
Silver	107·7	10·5	10·2	Calcium	40	1·58	25
Gold	196·2	19·34	10·1	Iodine	126·5	4·95	25·5
Aluminium	27·3	2·67	10·26	Bromine, *liquid*	79·75	3·19	25·0
Molybdenum	95·6	8·6	11·1	Chlorine, *liquid*	35·4	1·33	26·6
Silicon, *graphitoïdal*	28	2·5	11·2	Strontium	87·2	2·54	34·4
Lithium	7	0·59	11·9	Potassium	39	0·86	45·6
Cadmium	111·6	8·7	12·9				
Uranium	240	18·4	13·2				
Arsenic	74·9	5·63	13·3				
Magnesium	23·9	1·74	13·8				

The numbers in the third column of this table do not exhibit the simplicity of relation which exists between the specific volumes

of gaseous bodies. There are, indeed, several causes which interfere with the existence, or at least with the observation, of such simple relations between the specific volumes of solid and liquid elements. In the first place, the densities of three of them, viz., mercury, bromine, and chlorine, are such as belong to them in the liquid state, whereas the densities assigned to all the others have been determined in the solid state. In solids, moreover, the density is greatly affected by the state of aggregation, whether crystalline or amorphous, and in dimorphous bodies each form has a density peculiar to itself. Further, as solids and liquids are variously affected by heat, each having a peculiar rate of expansion, and that rate being different at different temperatures, it is not to be expected that their specific volumes should exhibit simple relations, unless they are compared at temperatures at which they are similarly affected by heat. Even gases are found to exhibit abnormal specific volumes if compared at temperatures too near the points at which they pass into the liquid state. In liquids, the simplest relations of specific volume are found at those temperatures for which the tensions of the vapours are equal (Kopp); and in solids, the melting points are most probably the comparable temperatures. Now the specific gravities of most of the solid elements in the preceding table have been determined at mean temperatures (as at 15·5°), which, in the case of potassium, sodium, phosphorus, and a few others, do not differ greatly from the melting points, but in other cases, as with gold, platinum, iron, &c., are removed from the melting points by very long intervals. In spite, however, of these causes of divergence, the specific volumes of certain analogous elements are very nearly equal to each other: viz., those of selenium and sulphur; of chromium, iron, cobalt, copper, manganese, and nickel; of molybdenum and tungsten; of iridium, platinum, palladium, and rhodium; and of gold and silver.

Specific Volumes of Solid and Liquid Compounds.—The most general relation that has been observed between the specific volumes of solid compounds, is that *isomorphous compounds have equal specific volumes*, in other words, that their densities are proportional to their molecular weights; such is the case, for example, with the native carbonates of strontium (strontianite) and of lead (cerussite):

Formula.	Molecular weight.	Specific gravity.	Specific volume.
$SrCO_3$	147·2	3·60	40·4
$PbCO_3$	266·4	6·47	41·2

If the crystalline forms are only approximately similar, the specific volumes also are only approximately equal, the difference being less as the angles of the two crystalline forms are more nearly equal and their axes more nearly in the same ratio. In dimorphous compounds, each modification has a density, and therefore a specific volume, peculiar to itself.

The hydrated sulphates of magnesium, zinc, nickel, cobalt, and

iron, which have the general formula, $M''SO_4 + 7H_2O$ (M'' denoting a bivalent metal: see next page), and crystallise in similar forms, have specific volumes very nearly equal to 146; the double sulphates isomorphous with potassio-cupric sulphate, $K_2Cu(SO_4)_2 + 6H_2O$, have specific volumes ranging between 198 and 216; and the alums, *e.g.*, $KAl(SO_4)_2 + 12H_2O$, have specific volumes ranging between 276 and 281.

The specific volumes of liquid compounds have been studied chiefly with relation to organic compounds. The most general relation observed is that: *Differences of specific volume are in numerous instances proportional to the differences between the corresponding chemical formulæ.* Thus liquids whose formulæ differ by nCH_2 differ in specific volume by n times 22; for example, methyl formate, $CH_3.CHO_2$, and ethyl butyrate, $C_2H_5.C_4H_7O_2$, which differ by $4CH_2$, have specific volumes differing by nearly 4×22.

Atomicity, Quantivalence.

We have seen that the atomic weight of an element is in some cases equal to its equivalent weight, in others, twice, three times, four times, &c., as great as the equivalent weight; in other words, an atom of certain elements can replace or be substituted for only one atom of hydrogen, whereas the atoms of other elements can replace 1, 2, 3, 4, &c., atoms of hydrogen. Thus, when sodium dissolves in hydrochloric acid, each atom of sodium replaces 1 atom of hydrogen; but when zinc dissolves in the same acid, each atom of zinc takes the place of 2 atoms of hydrogen: thus

$$\begin{aligned} Na + HCl &= NaCl + H \\ Zn + 2HCl &= ZnCl_2 + H_2 \end{aligned}$$

Here it is seen that an atom of zinc is equal in combining, or saturating power to 2 atoms of hydrogen. In like manner, antimony and bismuth form trichlorides, $AlCl_3$ and $BiCl_3$, in which the atom of the metal performs the same chemical function as 3 atoms of hydrogen, that is to say, it saturates 3 atoms of chlorine; so also tin in the tetrachloride is equivalent to 4H, and phosphorus in the pentachloride, PCl_5, to 5H.

This difference of equivalent, combining or saturating power, is called quantivalence or atomicity, and is sometimes denoted by placing dashes or Roman numerals to the right of the symbol of an element, and at the top, as O'', B''', C^{iv}, &c.; and the several elements are designated as—

Univalent	elements, or	Monads,	as H
Bivalent	,,	Dyads	,, O''
Trivalent	,,	Triads,	,, B'''
Quadrivalent	,,	Tetrads,	,, C^{iv}
Quinquivalent	,,	Pentads,	,, P^{v}
Sexvalent	,,	Hexads,	,, W^{vi}.

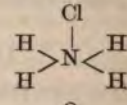
Elements of even equivalency, viz., the dyads, tetrads, and hexads, are also included under the general term artiads,* and those of uneven equivalency, viz., the monads, triads, and pentads, are designated generally as perissads.†

Another method of indicating the equivalent values of the elementary atoms, and the manner in which they are satisfied by combination, is to arrange the symbols in diagrams in which each element is connected with others by a number of lines, or connecting bonds corresponding with its degree of equivalence ; a monad being connected with other elements by only one such bond, a triad by three, a hexad by six, &c., as in the following examples :—

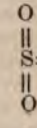
Water, H_2O . . . . . H—O—H

Carbon dioxide, CO_2 . . . . . O=C=O

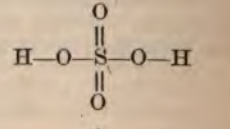
Ammonium chloride, NH_4Cl . .



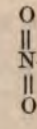
Sulphuric oxide, SO_3 . . . .



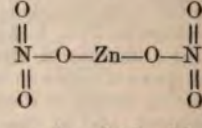
Sulphuric acid, H_2SO_4 . .



Nitric acid, HNO_3 . . . .



Zinc nitrate, ZnN_2O_6 . . .



In most cases, however, these formulæ may be abridged by the use of dots instead of dashes, thus

H . O . H	O : C : O	O.H O : N : O
Water.	Carbon dioxide.	Nitric acid.

* Αρτιος, even. † Περισσός, uneven.

It must be distinctly understood that these formulæ—which are called graphic, structural, or constitutional formulæ—are not intended to represent the actual arrangement of the atoms in a compound; indeed, even if we had a distinct notion of the manner in which the atoms of any compound are arranged, it could not be adequately represented on a plane surface. The lines connecting the different atoms indicate nothing more than the number of units of equivalency belonging to the several atoms, and the manner in which they are disposed of by combination with those of other atoms. Thus the formula for nitric acid indicates that two of the three constituent oxygen-atoms are combined with the nitrogen alone, and are consequently attached to that element by both their units of equivalency, whereas the third oxygen-atom is combined both with nitrogen and with hydrogen.

By inspection of the preceding diagrams, it will be observed that every atom of a compound has each of its units of equivalency satisfied by combination with a unit belonging to some other atom. Such, indeed, is the case in every saturated or normal compound. Accordingly, it is found that in all such compounds the sum of the perissad elements is always an even number. Thus a compound may contain two, four, six, &c., monad atoms, as ClH, OH_2, CH_4, C_2H_6, C_3H_8, SiH_3Cl; or one triad atom and three monads as BCl_3: or one pentad and five monads, as NH_4Cl; but never an uneven number of perissad atoms. This is the "law of even numbers," announced some years ago by Gerhardt and Laurent as a result of observation. It was long received with doubt, but has now been confirmed by the analysis of so many well-defined compounds, that a departure from it is looked upon as a sure indication of incorrect analysis.

For a similar reason, the atoms of elementary bodies rarely exist in the free state, but when separated from any compound, tend to combine with other atoms, either of the same or of some other element. Perissad elements, like hydrogen, chlorine, nitrogen, &c., separate from their compounds in pairs; their molecule contains two atoms, *e.g.*, H—H. Artiad elements may unite in groups of two, three, or more; thus the molecule of oxygen, in its ordinary state, probably contains two atoms, that of ozone three atoms; thus—

Oxygen . . . . . O=O

Ozone . . . . . O—O
\
O

The tendency of elementary atoms to separate in groups is shown in various ways. Thus when copper hydride, Cu_2H_2 (to be hereafter described), is decomposed by hydrochloric acid, a quantity of hydrogen is given off equal to twice that which is contained in the hydride itself; thus—

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2HH.$$

This action is precisely analogous to that of hydrochloric acid on cuprous oxide:

$$Cu_2O + 2HCl = Cu_2Cl_2 + H_2O.$$

In the latter case, the hydrogen separated from the hydrochloric acid unites with oxygen, in the former with hydrogen. Again, when solutions of sulphurous acid and sulphydric acid are mixed, the whole of the sulphur is precipitated:

$$H_2SO_3 + 2H_2S = 3H_2O + SS_2,$$

the action being similar to that of sulphurous acid on selenhydric acid:

$$H_2SO_3 + 2H_2Se = 3H_2O + SSe_2.$$

In the one case, a sulphide of selenium is precipitated; in the other, a sulphide of sulphur. The precipitation of iodine, which takes place on mixing hydriodic acid with iodic acid, affords a similar instance of the combination of homogeneous atoms:

$$5HI + HIO_3 = 3H_2O + 3II.$$

Another striking illustration of this mode of action is afforded by the reduction of certain metallic oxides by hydrogen dioxide. When silver oxide is thrown into this liquid, water is formed, the silver is reduced to the metallic state, and a quantity of oxygen is evolved equal to twice that which is contained in the silver oxide:

$$Ag_2O + H_2O_2 = H_2O + Ag_2 + OO.$$

Further, elementary bodies frequently act upon others as if their atoms were associated in binary groups. Thus chlorine acting upon potassium oxide forms two compounds, the chloride and hypochlorite of potassium (p. 179):

$$ClCl + KKO = KCl + KClO.$$

Again, in the action of chlorine upon many organic compounds, one atom of chlorine removes one atom of hydrogen as hydrochloric acid, while another atom of chlorine takes the place of the hydrogen thus removed. For example, in the formation of chloracetic acid by the action of chlorine on acetic acid:

$$C_2H_4O_2 + ClCl = HCl + C_2H_3ClO_2.$$

Similarly, when metallic sulphides oxidise in the air, both the metal and the sulphur combine with oxygen; and sulphur acting upon potash forms both a sulphide and a thiosulphate. In all these cases the atoms of the elementary bodies act in pairs.

On the supposition that the molecules of elementary bodies in the gaseous state are made up of two atoms, the specific volumes

of these gases will come under the same law as that which applies to compounds (p. 278): and it may then be stated generally, that, with the few exceptions already noticed, *the specific gravities of all bodies, simple and compound, in the gaseous state, are equal to half their molecular weights;* or the *specific volumes* (the quotients of the molecular weights by the specific gravities) *are equal to* 2.

There are, however, two elements, namely, phosphorus and arsenic, which at all temperatures hitherto attained exhibit a vapour-density twice as great as that which they should have according to the general law, that of phosphorus being always 61·9, and that of arsenic 149·8. This has been explained by supposing that the molecule of each of these two elements in the free state contains four atoms instead of two, as is the case with most elementary bodies; thus the molecule of phosphorus is supposed to be represented by the formula,

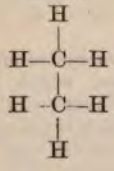
Variation of Equivalency.—Multivalent elements often exhibit varying degrees of equivalency. Thus carbon, which is quadrivalent in marsh gas, CH_4, and in carbon dioxide, CO_2, is only bivalent in carbon monoxide, CO; nitrogen, which is quinquivalent in sal-ammoniac, NH_4Cl, and the other ammonium salts, and in nitrogen pentoxide, N_2O_5, is trivalent in ammonia, NH_3, and in nitrogen trioxide, N_2O_3, and univalent in nitrogen monoxide, N_2O; sulphur, also, which is sexvalent in sulphur trioxide, SO_3, is quadrivalent in sulphur dioxide, SO_2, and bivalent in hydrogen sulphide, H_2S, and in many metallic sulphides. In these cases, and in others of varying equivalency, the variation mostly takes place by two units of equivalency. It is not very easy to account for these variations; but it is observed in all cases that the compounds in which the equivalency of a polygenic element is most completely satisfied are more stable than the others, and that the latter tend to pass into the former by taking up the required number of univalent or bivalent atoms; thus, carbon monoxide, CO, easily takes up another atom of oxygen to form the dioxide, CO_2; nitrogen trioxide, N_2O_3, is readily converted into the pentoxide, N_2O_5; ammonia, NH_3, unites readily with hydrochloric acid to form sal-ammoniac, NH_4Cl, &c. Similar phenomena are exhibited by many organo-metallic bodies, as will be explained further on.

From this it seems most probable that the true quantivalence of a polygenic element is that which corresponds with the maximum number of monad atoms with which it can combine, but that one or two pairs of its units of equivalency may, under certain circumstances, remain unsaturated. Whether a saturated or an unsaturated compound is formed, will depend on a variety of conditions, often in great measure on the relative quantities of the acting substances.

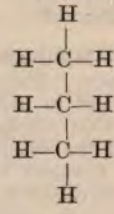
Thus phosphorus, which is a pentad element, forms with chlorine either a trichloride, PCl_3, or a pentachloride, PCl_5, according as the phosphorus or the chlorine is in excess (p. 228).

In compounds containing two or more atoms of the same multivalent element, one or more units of equivalence belonging to each of these atoms may be neutralised by combination with those of another atom of the same kind, so that the element in question will appear to enter into the compound with less than its normal degree of equivalence. Thus in ethane, or dimethyl, C_2H_6, which is a perfectly stable compound, having no tendency to take up an additional number of atoms of hydrogen or any other element, the carbon appears to be trivalent instead of quadrivalent; similarly in propane, C_3H_8, its equivalence appears to be reduced to $\frac{8}{3}$; and in butane or diethyl, C_4H_{10}, to $\frac{5}{2}$. In all these cases, however, the diminution of equivalent value in the carbon-atoms is only apparent, as may be seen from the following formulæ:

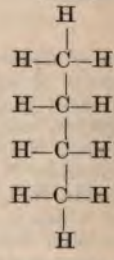
Ethane.



Propane.



Butane.



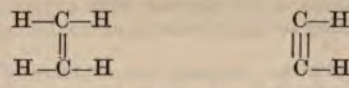
or, more shortly, omitting the equivalent marks of the monad atoms:

$H_3C.CH_3$ Ethane. $H_3C.CH_2.CH_3$ Propane. $H_3C.CH_2.CH_2.CH_3$ Butane.

In each of these compounds, every carbon-atom, except the two outside ones, has two of its units of equivalence satisfied by combination with those of the neighbouring carbon-atoms, while each of the two exterior ones has only one unit thus satisfied. Hence, in any similarly constituted compound containing n carbon-atoms, the number of units of equivalence remaining to be satisfied by the hydrogen-atoms is $4n-2(n-2)-2=2n+2$. The general formula of this series of hydrocarbons is, therefore, C_nH_{2n+2}, and the equivalent value of the carbon is $\frac{2n+2}{n}$.

In other cases, multivalent atoms may be united by two or more of their units of equivalence, so that their combining power may appear to be still further reduced, as in the hydrocarbon, C_2H_4, in

which the carbon may be apparently bivalent, and in C_2H_2, in which it may appear to be univalent; thus—



Sometimes also the apparent alteration of combining capacity may be due to the fact that the simplest formula by which a compound may be represented is not its true molecular formula. For example, the two chlorides of tin are usually represented by the formulæ $SnCl_2$ and $SnCl_4$. The second of these is undoubtedly correct, that is to say, the molecule of stannic chloride, as shown by its vapour-density, contains 1 atom of tin and 4 atoms of chlorine (p. 277), and consequently tin is a tetrad or quadrivalent element. But the lower chloride, in which the tin appears to be only bivalent, should in all probability be represented by a higher formula: for this compound is much less volatile than stannic chloride, requiring a bright red heat to vaporise it, and at the same time undergoing partial decomposition, whereas stannic chloride volatilises without decomposition at 120°. Hence it may be inferred that the molecule of stannous chloride is heavier and more complex than that of stannic chloride, and should therefore be represented by the double formula Sn_2Cl_4 or $Cl_2Sn{=}SnCl_2$, in which the tin still figures as a tetrad, though relatively to the chlorine it is only bivalent.

In most cases, the quantivalence or atomicity of an element is most safely determined by the number of monad atoms with which it can combine. Of dyad atoms, indeed, any element or compound may take up an indefinite number, without alteration of its quantivalence or combining power: for each dyad atom, possessing two units of equivalency, neutralises one unit in the compound which it enters, and introduces another, leaving, therefore, the combining power of the compound just what it was before. Thus potassium forms only one chloride, KCl, and is therefore univalent or monadic; but in addition to the oxide, K_2O, corresponding with this chloride, it likewise forms two others, viz., K_2O_2 and K_2O_4, in the former of which it might be regarded as dyadic, and in the latter as tetradic; but the manner in which dyad oxygen enters these compounds is easily seen by inspection of the following diagrams:—

K.O.K	K.O.O.K	K.O.O.O.OK.
Monoxide.	Dioxide.	Tetroxide.

It is evident that any number of oxygen-atoms might, in like manner, be inserted without disturbing the balance of equivalency. If, indeed, we turn to the sulphides of potassium, in which the sulphur is dyadic, like oxygen, we find the series, K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5, the constitution of which may be represented in a precisely similar manner. Hence the quantivalence of any element is, for the most part, best determined by the composition of its

chlorides, bromides, iodides, or fluorides, rather than by that of its oxides or sulphides. In some cases, however, as will be seen further on, the combinations of an element with oxygen afford the best means of determining its quantivalence or combining capacity.

Compound Radicles.—Suppose one or more of the component atoms of a fully saturated molecule to be removed: it is clear that the remaining atom or group of atoms will no longer be saturated, but will have a combining power corresponding with the number of units of equivalency removed. Such unsaturated groups are called residues or radicles. Methane, CH_4, is a fully saturated compound; but if one of its hydrogen-atoms be removed, the residue CH_3 (called methyl), will be ready to combine with one atom of a univalent element, such as chlorine, bromine, &c., forming the compounds CH_3Cl, CH_3Br, &c.; two atoms of it unite in like manner with one atom of oxygen, sulphur, and other bivalent elements, forming the compounds $O''(CH_3)_2$, $S''(CH_3)_2$, &c.; three atoms with nitrogen yielding $N'''(CH_3)_3$, &c.

The removal of two hydrogen-atoms from CH_4 leaves the bivalent radicle CH_2, called methylene, which yields the compounds CH_2Cl_2, CH_2O, CH_2S, &c. The removal of three hydrogen-atoms from CH_4 leaves the trivalent radicle CH, which, in combination with three chlorine-atoms, constitutes chloroform, $CHCl_3$. And, finally, the removal of all four hydrogen-atoms from CH_4 leaves the quadrivalent radicle carbon, capable of forming the compounds CCl_4, CS_2, &c.

In like manner, *ammonia*, NH_3, in which the nitrogen is trivalent, yields, by removal of one hydrogen-atom, the univalent radicle amidogen, NH_2, which with one atom of potassium forms potassamine, NH_2K, and when combined with one atom of the univalent radicle methyl, CH_3, forms methylamine, $NH_2(CH_3)$, &c. The abstraction of two hydrogen-atoms from the molecule NH_3, leaves the bivalent radicle imidogen, NH, which with two methyl-atoms forms dimethylamine, $NH(CH_3)_2$, &c.; and the removal of all three hydrogen-atoms from NH_3, leaves nitrogen itself, which frequently acts as a trivalent element or radicle, forming tripotassamine, NK_3, trimethylamine, $N(CH_3)_3$, &c.

Finally, the molecule of *water*, OH_2, by losing an atom of hydrogen, is converted into the univalent radicle hydroxyl, OH, which, in its relations to other bodies, is analogous to chlorine, bromine, and iodine, and may be substituted in combination for one atom of hydrogen or other monads. Thus, water itself may be regarded as H.OH, analogous to hydrochloric acid, HCl; potassium hydroxide as K.OH, analogous to potassium chloride; barium hydroxide, as $Ba(OH)_2$, analogous to barium chloride, $BaCl_2$.

In a similar manner, the univalent radicle, potassoxyl, KO, may be derived from potassium hydroxide; the bivalent radicle, zincoxyl, ZnO_2, by abstraction of H_2 from zinc hydroxide, $Zn''H_2O_2$. The essential character of these oxygenated radicles is

that each of the oxygen-atoms contained in them is united to the other atoms by one unit of equivalency only, so that the radicle has necessarily one or two units unconnected ; thus—

Hydroxyl	H—O—
Potassoxyl	K—O—
Zincoxyl . . .	—O—Zn—O—

From the preceding explanations of the mode of derivation of compound radicles, it is clear that there is no limit to the number of them which may be supposed to exist ; in fact, it is only necessary to suppose a number of units of equivalency abstracted from any saturated molecule, in order to obtain a radicle of corresponding combining power or equivalent value. But unless a radicle can be supposed to enter into a considerable number of compounds, thus forming them into a group, like the salts of the same metal, there is nothing gained in point of simplicity or comprehensiveness by assuming its existence.

It must also be distinctly understood that these compound radicles do not necessarily exist in the separate state, and that those of uneven equivalency, like methyl, cannot exist in that state, their molecules, if liberated from combination with others, always doubling themselves, as we have seen to be the case with most of the elementary bodies. Thus hydroxyl —O—H is not known in the free state, the actually existing compound containing the same proportions of hydrogen and oxygen being O_2H_2 or H—O—O—H. In like manner methyl, CH_3, has no separate existence, but dimethyl, C_2H_6, is a known compound :—

Methyl. Dimethyl.

Relations between Atomic Weight and Quantivalence.—A very remarkable relation has been shown to exist between the quantivalence of the elements and the numerical order of their atomic weights. Arranging the elements in horizontal lines according to this order, as in the following table (in which the atomic weights are, for the most part, represented by their nearest whole numbers) we find that, with the exception of certain metals belonging to the iron and platinum groups, they all arrange themselves in such a manner, that the first vertical column is occupied by the monad elements, the second by the dyads, the third by the triads, &c., as indicated by the headings of the columns, in which the symbol R stands for a metal. Hydrogen stands alone, there being no known element intermediate between it and the monad metal lithium. This relation of the elementary bodies, which is called the "periodic law," was first pointed out by Newlands in 1864, and afterwards developed by Odling, Lothar Meyer, and Mendelejeff.

Series.	Group I. R_2O.		II. RO.		III. R_2O_3.		IV. RH_4. RO_2.	V. RH_3. RO_5.		VI. RH_2. RO_3.		VII. RH_7. R_2O_7.		VIII. RO_4.		
1	H. 1															
2	Li 7		Be 9	—	B 11	—	C 12	N 14	—	O 16	—	F 19				
3	Na 23		Mg 24		Al 27·3	—	Si 28	P 31	—	S 32	—	Cl 35·4				
4	K 39		—	Ca 40	—	Sc 44	Ti 48	—	V 51	—	Cr 52·4	—	Mn 55	Fe 56	Ni 59	Co 59
5	—	Cu 63	Zn 65	—	Ga 69·8	—	—	As 75	—	Se 79	—	Br 80	—			
6	Rb 85	—	—	Sr 87	—	Y 89	Zr 90	—	Nb 94	—	Mo 95·6	—	—	Ru 103·5	Rh 104	Pd 106
7	—	Ag 108	Cd 111·6	—	In 113·4	—	Sn 118	Sb 122	—	Te 128?	—	I 126	—			
8	Cs 133	—	—	Ba 137	—	La 139	Ce 141·2	Di 147	Ta 182	—	W 184	—	—	Os 199	Ir 197	Pt 197
9	—	Au 196	Hg 200	—	Tl 204	—	Pb 206	Bi 210	—	—	—					
10	—	—	—	—	—	—	Th 231·5				U 240					

The elements in each of the first seven groups of this table (except the fourth) range themselves naturally in two columns, each composed of elements closely related to one another in their chemical properties; thus in Group I, the left-hand column contains the alkali-metals, lithium, sodium, &c., while the right-hand column includes the metals copper, silver, and gold, which exhibit considerable analogy in their chemical relations, each forming two chlorides, oxides, &c. Again in Group VI, the first column is formed by the closely related non-metallic elements, oxygen, sulphur, selenium, and tellurium, while the second contains the metals chromium, molybdenum, tungsten, and uranium, which also greatly resemble one another in their chemical relations.

Of the elements in the first group, the alkali-metals, Li, Na, K, &c., are shown to be univalent, by their combination with chlorine and oxygen, *e.g.*, NaCl, and $\frac{Na}{Na}>O$. Copper may be regarded as univalent in one series of its compounds, viz., the cuprous compounds, as in the chloride CuCl or Cu_2Cl_2, and the oxide Cu_2O, though in its most stable compounds it is bivalent, and appears to be more nearly related to the metals of the iron group. The place of gold in the series is somewhat exceptional, since, though univalent in the aurous compounds, as AuCl, it is trivalent in the more stable auric compounds, as $AuCl_3$.

The elements in Group II are all dyads.

Of the elements in Group III, column 1, boron, gallium, indium, and thallium, are undoubtedly triads. Aluminium forms a trichloride, $AlCl_3$, and a corresponding oxide, Al_2O_3; also a volatile methyl-compound, $Al(CH_3)_3$, the vapour-density of which indicates that the molecule, as represented by this formula, has the normal 2-volume condensation (p. 278). It is true that the chloride, which is also volatile, exhibits a vapour-density agreeing rather with the doubled formula, Al_2Cl_6, which would indicate that aluminium is a tetrad, the chloride having the constitution $Cl_3Al.AlCl_3$; but this chloride boils at a very high temperature, and it is therefore probable that the temperature at which its vapour-density was actually determined was not sufficiently raised above the boiling point to bring the compound into the state of a perfect gas (p. 278).

The rare earth-metals in Group III, column 2, have been lately shown to be triads, forming trichlorides and sesquioxides. All the elements in Group IV have long been classed as tetrads, with the exception of cerium, the quantivalence of which was till lately regarded as doubtful; but the recent experiments of Dr. Brauner have decidedly shown that it is a tetrad.

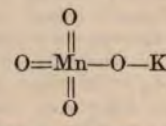
Of the elements in Group V, phosphorus, antimony, niobium, and tantalum form pentachlorides. Nitrogen is quinquivalent in the ammonium-compounds, as in the chloride NH_4Cl. Vanadium, arsenic, and bismuth do not combine with more than 3 atoms of chlorine, bromine, or iodine; but bismuth forms an oxychloride, $BiOCl_3$, in which it is quinquivalent, and vanadium forms the

analogous compound, $VOCl_3$. Arsenic does not form a similar oxychloride; but its highest oxide, As_2O_5, is the exact analogue of phosphoric oxide, P_2O_5, and vanadic oxide, V_2O_5, and forms a series of salts, the arsenates, which are isomorphous with the phosphates and vanadates. For these reasons arsenic is likewise regarded as a pentad.

Among the elements in Group VI, chromium forms a hexfluoride and tungsten a hexchloride; uranium forms an oxychloride, UO_2Cl_2, and a trioxide, UO_3. Sulphur, selenium, and tellurium, so far as regards their hydrogen-compounds, H_2S, &c., are dyads; but with regard to their combinations with chlorine, they are tetrads, and sulphur is known to form certain organic compounds in which it is tetradic, and others in which it is hexadic.* Moreover the chemical relations of the sulphates are much more clearly represented by formulæ in which sulphur is supposed to be hexadic, like that given for sulphuric acid on p. 282, than by formulæ into which it enters as a dyad, such as, H—O—O—S—O—O—H, inasmuch as compounds in which dyadic elements are linked together in one row, are for the most part very unstable, like the higher oxides and sulphides of potassium (p. 287). These three elements are therefore best regarded as hexads, though they sometimes enter into combination as tetrads, and very frequently as dyads.

Oxygen, in its combinations with hydrogen, and with most of the metals is undoubtedly bivalent; but it appears also to be capable of higher degrees of combination; with silver, for example, it forms the two oxides Ag_2O and Ag_4O, in the latter of which it is quadrivalent; and from its close analogies to sulphur, and the place of its atomic weight in the series, it may be classed with the hexads.

Of the elements in Group VII, manganese appears to form a heptachloride, $MnCl_7$, though the composition of this chloride has not perhaps been very distinctly made out; but in the permanganates the metal appears to be decidedly septivalent; the potassium salt, $KMnO_4$, for example, may be represented by the structural formula:



The perchlorates, *e.g.*, $KClO_4$, are similar to the permanganates in composition and in crystalline form, and may therefore be supposed

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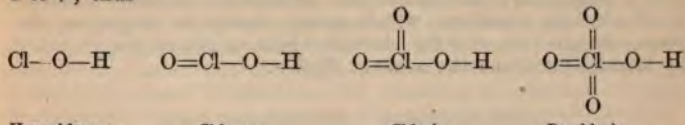
* Sulphur triethiodide, $S^{IV}\left\{\begin{matrix}(C_2H_5)_3\\ I\end{matrix}\right.$

Sulphur diethylene-dibromide, $S^{VI}\left\{\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ Br_2\end{matrix}\right.$

to have a similar constitution, the chlorine in them being septivalent; in fact, the four oxy-acids of chlorine form a regular series in which the quantivalence of the chlorine varies by two units from 1 to 7; thus—



Hypochlorous. Chlorous. Chloric. Perchloric.

Iodic acid, IO_3H, and periodic acid, IO_4H, are exactly similar in constitution to chloric and perchloric acids, and the corresponding oxides or anhydrides I_2O_5, I_2O_7 are likewise known (p. 182): hence iodine also may be regarded as a heptad. Bromic acid, BrO_3H, is similar to chloric acid, but the existence of perbromic acid is doubtful, and of fluorine no oxygen-compound is known; but from the close analogy in the reactions of these four elements, Cl, Br, I, and F, and the manner in which they replace one another in combination, there can be no doubt that they belong to the same group. In their combinations with hydrogen, and in the reactions in which they replace hydrogen and one another in combination, they invariably act as monads, the substitution taking place atom for atom.

Lastly, with regard to the elements (all metallic) which cannot be included in either of the seven groups above considered. The atomic weights of three of these metals, viz., iron, cobalt, and nickel, have values between those of manganese and copper; and of the other six, called platinum metals, three, viz., ruthenium, rhodium, and palladium, have atomic weights intermediate between those of molybdenum (96) and silver (108), while those of the other three, viz., osmium, iridium, and platinum, are greater than that of tungsten and nearly equal to that of gold.

These intermediate elements, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, constitute a group of themselves (the eighth), some of the members of which, viz., Ru and Os, form tetroxides (analogous to octochlorides) and may therefore be regarded as octads. None of these metals indeed form chlorides containing more than four atoms of chlorine, but four of them, viz., Pt, Ir, Ru, and Os, form with the alkali-metals double chlorides in which the platinum, &c., is united with eight univalent atoms, *e.g.*, potassium platinochloride,

$$Cl_4Pt(NaCl)_2.$$

The blank spaces in the preceding table indicate the places of elements which probably exist, but have not yet been discovered. Several anticipated discoveries of this kind have however been actually realised. When the table was drawn up, a blank in the space now occupied by gallium indicated the probable existence of a trivalent element intermediate in atomic weight between zinc and

arsenic. This element was provisionally designated *Ekaluminium* by Mendelejeff, who predicted from its position in the series, what its chief properties ought to be. The discovery of gallium with the atomic weight 69·8 has verified this prediction. Another example is afforded by scandium, which agrees closely in properties and atomic weight (44) with the element whose existence was predicted by Mendelejeff under the name of *Ekabor*.

CRYSTALLISATION ; CRYSTALLINE FORM.

Almost every substance, simple or compound, capable of existing in the solid state, assumes, under favourable circumstances, a distinct geometrical figure, usually bounded by plane surfaces, and having angles of constant value. The faculty of crystallisation seems to be denied only to a few bodies, chiefly highly complex organic principles, which stand, as it were, upon the very verge of organisation, and which, when in the solid state, are frequently characterised by a kind of beady or globular appearance, well known to microscopical observers.

The most beautiful examples of crystallisation are to be found among natural minerals, the results of exceedingly slow changes constantly occurring within the earth. It is invariably found that artificial crystals of salts, and other soluble substances which have been slowly and quietly deposited, surpass in size and regularity those of more rapid formation.

Solution in water or some other liquid is a very frequent method of effecting crystallisation. If the substance be more soluble at a high than at a low temperature, then a hot and saturated solution left to cool slowly will generally be found to furnish crystals : this is a very common case with salts and various organic principles. If it be equally soluble, or nearly so, at all temperatures, then slow spontaneous evaporation in the air, or over a surface of oil of vitriol, often proves very effective.

Fusion and slow cooling may be employed in many cases : that of sulphur is a good example : the metals, when thus treated, usually afford traces of crystalline figure, which sometimes become very beautiful and distinct, as with bismuth. A third condition under which crystals very often form is in passing from the gaseous to the solid state, of which iodine affords a good instance. When by any of these means time is allowed for the symmetrical arrangement of the particles of matter at the moment of solidification, crystals are produced.

That crystals owe their figure to a certain regularity of internal structure is shown both by their mode of formation and also by the peculiarities attending their fracture. A crystal placed in a slowly evaporating saturated solution of the same substance, grows or increases by a continued deposition of fresh matter upon its sides, in such a manner that the angles formed by the meeting of the latter remained unaltered.

The tendency of most crystals to split in particular directions, called by mineralogists *cleavage*, is a certain indication of regular structure, while the optical properties of many among them, and their mode of expansion by heat, point to the same conclusion.

It may be laid down as a general rule that every substance has its own crystalline form, by which it may very frequently be recognised at once—not that each substance has a different figure, although very great diversity in this respect is to be found. Some forms are much more common than others, as the cube and six-sided prism, which are very frequently assumed by a number of bodies not in any way related.

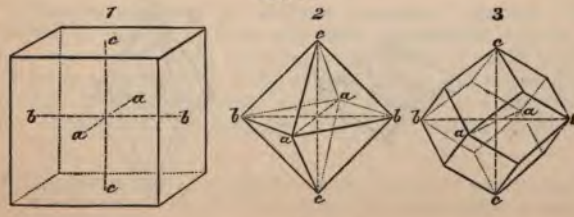
The same substance may assume, under different sets of circumstances, as at high and low temperatures, two different crystalline forms, in which case it is said to be *dimorphous*. Sulphur and carbon furnish, as already noticed, examples of this curious fact; another case is presented by calcium carbonate in the two modifications of calcspar and arragonite, both chemically the same, but physically different. A fourth example is presented by mercuric iodide, which also has two distinct forms, and even two distinct colours, the contrast between the two modifications being indeed as great as that between diamond and graphite.

Crystallographic Systems.—When a crystal of simple form is attentively considered, it becomes evident that certain directions can be pointed out in which straight lines may be imagined to be drawn, passing through the central point of the crystal from side to side, from end to end, or from one angle to that opposed to it, &c., about which lines the particles of matter composing the crystal may be conceived to be symmetrically built up. Such lines, or *axes*, are not always purely imaginary, however, as may be inferred from the remarkable optical properties of many crystals: upon their number, relative lengths, position, and inclination to each other, depends the outward figure of the crystal itself.

All crystalline forms may upon this plan be arranged in six classes or systems; these are the following.

1. **The monometric, regular, or cubic system** (fig. 128).—The crystals of this division have three equal axes, all placed at

Fig. 128.



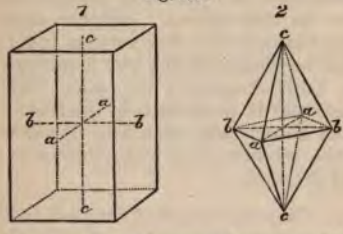
right angles to each other. The most important forms are the *cube* (1), *the regular octohedron* (2), and the *rhombic dodecahedron* (3).

The letters *a*—*a*, *b*—*b*, *c*—*c* (fig. 128), show the termination of the three axes, placed as stated.

Very many substances, both simple and compound, assume these forms, as most of the metals, carbon in the state of diamond, common salt, potassium iodide, the alums, fluor-spar, iron bisulphide, garnet, spinelle, &c.

2. The dimetric, quadratic, square prismatic, or pyramidal system.—The crystals of this system (fig. 129) are also symmetrical about three axes at right angles to each other. Of these, however, two only are of equal length, the third, *c*—*c*, being longer or shorter. The most important forms are, the *right square prism* (1), and the *right square-based octohedron* (2).

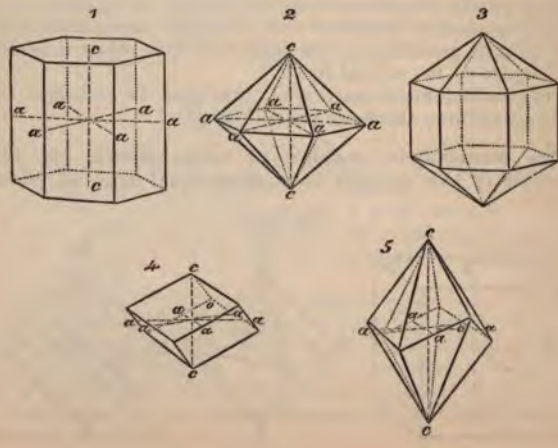
Fig. 129.



Examples of these forms are to be found in zircon, native stannic oxide, apophyllite, yellow potassium ferrocyanide, &c.

3. The rhombohedral system (fig. 130).—This is very impor-

Fig. 130.



tant and extensive ; it may be characterised by *four* axes,* three of which are equal, in the same plane, and inclined to each other at angles of 60°, while the fourth or principal axis is perpendicular to them all. The principal forms are,—the *regular six-sided prism* (1), the *regular double six-sided pyramid* (2), the *rhombohedron* (4), and the *scalenohedron* (5), a figure bounded by twelve scalene triangles.

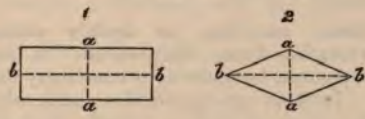
Examples are found in ice, calcspar, sodium nitrate, beryl, quartz or rock-crystal, and the semi-metals, arsenic, antimony, and tellurium.

A combination of the regular six-sided prism and double six-sided pyramid (3) is a common form of quartz.

4. **The trimetric, rhombic, or right prismatic system.**—This is characterised by three axes of unequal lengths, placed at right angles to each other, as in the *right rectangular prism*, the *right rhombic prism*, the *right rectangular-based octohedron*, and the *right rhombic-based octohedron.*

The bases of these forms are represented in fig. 131, (1) and (2). Let the reader imagine a straight line passing through the centre

Fig. 131.



of each of these figures, perpendicular to the plane of the paper ; this will represent the vertical axis. The octohedrons will be formed by joining the ends of this vertical line with the angles of the bases, and the prisms by vertical planes passing through the sides of the base, and terminated by horizontal planes passing through the extremities of the vertical axis. The perspective forms of these trimetric prisms and octohedrons are similar to those of the dimetric system (fig. 129).

The system is exemplified in sulphur crystallised at a low temperature, arsenical iron pyrites, potassium nitrate and sulphate, barium sulphate, &c.

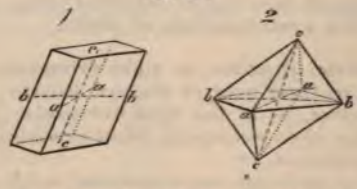
5. **The monoclinic or oblique prismatic system.**—Crystals belonging to this group have also three axes, which may be all unequal ; two of these (the secondary) are placed at right angles, the third being so inclined as to be oblique to one and perpendicular to the other. To this system may be referred the four following forms :—*The oblique rectangular prism*, the *oblique rhombic prism*,

* This reference to *four* axes is a mere matter of convenience ; *three* axes are sufficient for the determination of any solid figure whatever.

the *oblique rectangular-based octohedron*, the *oblique rhombic-based octohedron*.

The bases of these monoclinic forms are identical in form with those of the trimetric system, fig. 132, (1) and (2). The principal axis may be represented by a line passing through the plane of the paper at the middle point, perpendicular to *a a*, and oblique to *b b*. The perspective forms are shown in fig. 132.

Fig. 132.



Such forms are taken by sulphur crystallised by fusion and cooling, by realgar, sulphate, carbonate and phosphate of sodium, borax, green vitriol, and many other salts.

6. **The triclinic, anorthic, or doubly oblique prismatic system.**—The crystalline forms comprehended in this division are, from their great apparent irregularity, exceedingly difficult to study and understand. In them are traced three axes, which may be all unequal in length, and are all oblique to each other, as in the *doubly-oblique prism*, and in the *doubly-oblique octohedron*. The perspective forms are similar to those of the monoclinic system.

Copper sulphate, bismuth nitrate, and potassium quadroxalate afford illustrations of these forms.

Primary and Secondary Forms.—If a crystal increase in magnitude by equal additions on every part, it is quite clear that its figure must remain unaltered ; but if, from some cause, this increase should be partial, the newly-deposited matter being distributed unequally, but still in obedience to certain definite laws, then alterations of form are produced, giving rise to figures which have a direct geometrical connection with that from which they are derived. If, for example, in the cube, a regular omission of successive rows of particles of matter in a certain order be made at each solid angle, while the crystal continues to increase elsewhere, the result will be the production of small triangular planes, which, as the process advances, gradually usurp the whole of the surface of the crystal, and convert the cube into an octohedron. The new planes are called *secondary*, and their production is said to take place by regular *decrements* upon the solid angles. The same thing may happen on the edges of the cube ; a new figure, the rhombic dodecahedron, is then generated. The modifications which

can thus be produced of the original or *primary* figure (all of which are subject to exact geometrical laws) are very numerous. Several

Fig. 133.

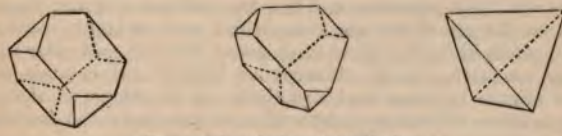
Passage of cube to octohedron.

distinct modifications may be present at the same time, and thus render the form exceedingly complex.

Crystals often cleave parallel to all the planes of the primary figure, as in calcspar, which offers a good illustration of this perfect cleavage. Sometimes one or two of these planes have a kind of preference over the rest in this respect, the crystal splitting readily in these directions only.

A very curious modification of the figure sometimes occurs by the excessive growth of each alternate plane of the crystal; the rest become at length obliterated, and the crystal assumes the

Fig. 134.



Passage of octohedron to tetrahedron.

character called *hemihedral* or *half-sided*. This is well seen in the production of the tetrahedron from the regular octohedron (fig. 134), and of the rhombohedric form by a similar change from the double six-sided pyramid (fig. 130, 2).

Forms belonging to the same crystallographic system are related to each other by several natural affinities.

1. *It is only the simple forms of the same system that can combine into a complex form.*—For in all fully developed (holohedral) natural crystals, it is found that all the similar parts, if modified at all, are modified in an exactly similar manner (in hemihedral forms, half the similar edges and angles alternately situated are similarly modified). Now this can be the case only when the dominant form and the modifying form are developed according to the same law of symmetry. Thus, if a cube and a regular octohedron are developed round the same system of axes, each summit of the cube is cut off to the same extent by a face of the octohedron, or *vice versâ*.

But a cube could never combine in this manner with a rhombic octohedron, because it would be impossible to place the two forms in such a manner that similar parts of the one should throughout replace similar parts of the other.

The crystals of each system are thus subject to a peculiar and distinct set of modifications, the observation of which very frequently constitutes an excellent guide to the discovery of the primary form itself.

2. *Crystals belonging to the same system are intimately related in their Optical properties.*—Crystals belonging to the regular system (as the diamond, alum, rock-salt, &c.) refract light in the same manner as uncrystallised bodies; that is to say, they have but one refractive index, and a ray of light passing through them in any direction is refracted singly. But all other crystals refract doubly, that is to say, a ray of light passing through them (except in certain directions) is split into two rays, the one called the *ordinary* ray, being refracted as it would be by an amorphous body, the other, called the *extraordinary* ray, being refracted according to peculiar and more complex laws (see LIGHT). Now, the crystals of the dimetric and hexagonal systems resemble each other in this respect, that in all of them there is one direction, called the optic axis, or axis of double refraction (coinciding with the principal crystallographic axis), along which a ray of light is refracted singly, while in all other directions it is refracted doubly; whereas in crystals belonging to the other systems, viz., the trimetric and the two oblique systems, there are always *two* directions or axes, along which a ray is singly refracted.

3. *Crystals belonging to the same system resemble each other in their mode of conducting heat.*—Amorphous bodies and crystals of the regular system conduct heat equally in all directions, so that, supposing a centre of heat to exist within such a body, the isothermal surfaces will be spheres. But crystals of the dimetric and hexagonal systems conduct equally only in directions perpendicular to the principal axis, so that in such crystals the isothermal surfaces are ellipsoïds of revolution round that axis; and crystals belonging to either of the three other systems conduct unequally in all directions, so that in them the isothermal surfaces are ellipsoïds with three unequal axes.

Relations of Form and Constitution; Isomorphism.

Certain substances, to which a similar chemical constitution is ascribed, possess the remarkable property of exactly replacing each other in crystallised compounds, without alteration of the characteristic geometrical figure. Such bodies are said to be *isomorphous.**

For example, magnesia, zinc oxide, cupric oxide, ferrous oxide,

* From ἴσος, equal, and μόρφη, shape or form.

and nickel oxide, are allied by isomorphic relations of the most intimate nature. The salts formed by these substances with the same acid and similar proportions of water of crystallisation, are identical in their form, and, when of the same colour, cannot be distinguished by the eye: the sulphates of magnesium and zinc may be thus confounded. These sulphates, too, all combine with potassium sulphate and ammonia sulphate, giving rise to double salts, whose figure is the same, but quite different from that of the simple sulphates. Indeed, this connection between identity of form and parallelism of constitution runs through all their combinations.

In the same manner alumina and iron sesquioxide replace each other continually without change of crystalline figure: the same remark may be made of the oxides of potassium, sodium, and ammonium. The alumina in common alum may be replaced by iron sesquioxide, the potash by ammonia or by soda, and still the figure of the crystal remains unchanged. These replacements may be partial only: we may have an alum containing both potash and ammonia, or alumina and chromium sesquioxide. By artificial management—namely, by transferring the crystal successively to different solutions—we may have these isomorphous and mutually replacing compounds distributed in different layers upon the same crystal.

For these reasons mixtures of isomorphous salts can never be separated by crystallisation, unless their difference of solubility is very great. A mixed solution of ferrous sulphate and nickel sulphate, isomorphous salts, yields on evaporation crystals containing both iron and nickel. But if before evaporation the ferrous salt be converted into ferric salt, by chlorine or other means, then the crystals obtained are free from iron, except that of the mother-liquor which wets them. The ferric salt is no longer isomorphous with the nickel salt, and easily separates from the latter.

Absolute identity of value in the angles of crystals is not always exhibited by isomorphous substances. In other words, small variations often occur in the magnitude of the angles of crystals of compounds which in all other respects show the closest isomorphic relations. This should occasion no surprise, as there are reasons why such variations might be expected, the chief perhaps being the unequal effects of expansion by heat, by which the angles of the same crystal are changed by alteration of temperature. A good example is found in the case of the carbonates of calcium, magnesium, manganese, iron, and zinc, which are found native crystallised in the form of obtuse rhombohedrons (fig. 130, 4), not distinguishable from each other by the eye, but exhibiting small differences in their angles when accurately measured. These compounds are isomorphous, and the measurements of the obtuse angles of their rhombohedrons are as follows :—

Calcium carbonate	. . . . .	105° 5′
Magnesium „	. . . . .	107° 25′
Manganous „	. . . . .	107° 20′
Ferrous „	. . . . .	107°
Zinc „	. . . . .	107° 40′

Anomalies in the composition of various earthy minerals, which formerly threw much obscurity upon their chemical nature, have been in great measure explained by these discoveries. Specimens of the same mineral from different localities were found to afford very discordant results on analysis. But the proof once given of the extent to which substitution of isomorphous bodies may go, without destruction of what may be called the primitive type of the compound, these difficulties vanish.

Decision of a doubtful point respecting the constitution of a compound may sometimes be very satisfactorily made by reference to its isomorphous relations, as in the case of alumina already mentioned, which is isomorphous with the sesquioxide of iron (p. 275).

The direct determination of the crystalline forms of the elementary bodies is often difficult, and the question of their isomorphism is complicated by the frequent dimorphism which they exhibit, but when compounds are found to correspond in chemical constitution and crystalline form, it may sometimes be inferred that the elements composing them are likewise isomorphous. Thus, the metals magnesium, zinc, iron, and copper are presumed to be isomorphous. Arsenic and phosphorus have not the same crystalline form; nevertheless they are said to be isomorphous, because arsenic and phosphoric acids give rise to combinations which agree most completely in figure and constitution. The chlorides, iodides, bromides, and fluorides agree, whenever they can be observed, in the most perfect manner: hence the elements themselves are believed to be isomorphous.

The subjoined table, taken with slight modification from Graham's "Elements of Chemistry,"* will serve to convey some idea of the most important families of isomorphous elements:

* Second edition, vol. i. p. 175.

Isomorphous Groups.

(1.)	(3.)	(6.)
Sulphur	Barium	Sodium
Selenium	Strontium	Silver
Tellurium	Lead	Thallium
		Gold
(2.)	(4.)	Potassium
Magnesium	Platinum	*Ammonium*
Calcium	Iridium	
Manganese	Osmium	(7.)
Iron		Chlorine
Cobalt	(5.)	Iodine
Nickel	Tin	Bromine
Zinc	Titanium	Fluorine
Cadmium	Zirconium	*Cyanogen*
Copper	Tungsten	
Chromium	Molybdenum	(8.)
Aluminium	Tantalum	Phosphorus
Glucinum	Niobium	Arsenic
		Antimony
		Bismuth
		Vanadium

A comparison of this table with that on page 290 will show that, in many instances, isomorphous elements exhibit equal quantivalence or combining capacity, and more generally that the isomorphous groups consist wholly of perissad or wholly of artiad elements. The only apparent exception to this rule is afforded by tantalum and niobium, which, although pentads, are isomorphous with tin, tungsten, and other tetrad and hexad elements.

CHEMICAL AFFINITY.

THE term Chemical Affinity, or Chemical Attraction, is used to describe that particular power or force, in virtue of which, union, often of a very intimate and permanent nature, takes place between two or more bodies, in such a way as to give rise to a *new* substance, having, for the most part, properties very different from those of its components.

The attraction thus exerted between different kinds of matter is to be distinguished from other modifications of attractive force which are exerted indiscriminately between all descriptions of substances, sometimes at enormous distances, sometimes at intervals quite inappreciable. Examples of the latter are to be seen in cases of which is called *cohesion*, when the particles of solid bodies are immovably bound together into a mass. Then there are other effects of, if possible, a still more obscure kind; such as the various actions of surface, the adhesion of certain liquids to glass, the repulsion of others, the ascent of water in narrow tubes, and a multitude of phenomena which are described in works on Physics, under the head of *molecular actions*. From all these, true chemical attraction may be at once distinguished by the deep and complete change of characters which follows its exertion: we might indeed define affinity to be a force by which new substances are generated.

Nevertheless, chemical combination graduates so imperceptibly into mere mechanical mixture, that it is often impossible to mark the limit. Solution is the result of a weak kind of affinity existing between the substance dissolved and the solvent—an affinity so feeble as completely to lose one of its most prominent features when in a more exalted condition—namely, power of causing elevation of temperature; for in the act of mere solution, the temperature falls, the heat of combination being lost and overpowered by the effects of change of state.

The force of chemical attraction thus varies greatly with the nature of the substances between which it is exerted; it is influenced, moreover, to a very large extent, by external or adventitious circumstances. An idea formerly prevailed that the relations of affinity were fixed and constant between the same substances, and great pains were taken in the preparation of tables exhibiting what was called the precedence of affinities. The order pointed out in these lists is now acknowledged to represent the order of precedence *for the circumstances* under which the experiments were made, but nothing more; so soon as these circumstances become changed, the order is disturbed. The ultimate effect, indeed, is not the result of the exercise of one single force, but rather the joint effect of a number, so complicated and variable in intensity, that in the

greater number of cases it is not possible to predict the consequences of a yet untried experiment.

It will be proper to examine shortly some of these extraneous causes to which allusion has been made, which modify to so great an extent the direct and original effects of the specific attractive force.

Alteration of temperature may be reckoned among these. When metallic mercury is heated nearly to its boiling point, and in that state exposed for a long time to the air, it absorbs oxygen, and becomes converted into a dark-red crystalline powder. This very same substance, when raised to a still higher temperature, separates spontaneously into metallic mercury and oxygen gas. It may be said, and probably with truth, that the latter change is greatly aided by the tendency of the metal to assume the vaporous state; but precisely the same fact is observed with another metal, palladium, which is not volatile, excepting at extremely high temperatures, but which oxidises superficially at a red heat, and again becomes reduced when the temperature rises to whiteness.

Insolubility and the power of vaporisation are perhaps, beyond all other disturbing causes, the most potent; they interfere in almost every reaction which takes place, and very frequently turn the scale when the opposed forces do not greatly differ in energy. It is easy to give examples. When a solution of calcium chloride is mixed with a solution of ammonium carbonate, double interchange ensues, calcium carbonate and ammonium chloride being generated: $CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl$. Here the action can be shown to be in a great measure determined by the insolubility of the calcium carbonate. On the other hand, when dry calcium carbonate is powdered and mixed with ammonium chloride, and the whole heated in a retort, a sublimate of ammonium carbonate is formed, while calcium chloride remains behind. In this instance, it is no doubt the great volatility of the new ammoniacal salt which chiefly determines the kind of decomposition.

When iron filings are heated to redness in a porcelain tube, and vapour of water is passed over them, the water undergoes decomposition with the utmost facility, hydrogen being rapidly disengaged, and the iron converted into oxide. On the other hand, oxide of iron, heated in a tube through which a stream of dry hydrogen is passed, suffers almost instantaneous reduction to the metallic state, while the vapour of water, carried forward by the current of gas, escapes as a jet of steam from the extremity of the tube. In these experiments the affinities between the iron and oxygen and the hydrogen and oxygen are so nearly balanced, that the difference of *atmosphere* is sufficient to settle the point. An atmosphere of steam offers little resistance to the escape of hydrogen; an atmosphere of hydrogen bears the same relation to steam; and this apparently trifling difference of circumstances is quite enough for the purpose.

What is called the *nascent state* is one very favourable to chemical

combination. Thus, nitrogen refuses to combine with gaseous hydrogen; yet when these substances are simultaneously liberated from some previous combination, they unite with great ease, as when organic matters are destroyed by heat, or by spontaneous putrefactive change.

There is a remarkable, and, at the same time, very extensive class of actions, grouped together under the general title of cases of *disposing affinity*. Metallic silver does not oxidise at any temperature; nay, more, its oxide is easily decomposed by simple heat; yet if the finely-divided metal be mixed with siliceous matter and alkali, and ignited, the whole fuses to a yellow transparent glass of silver silicate. Platinum is attacked by fused potassium hydrate, hydrogen being probably disengaged while the metal is oxidised: this is an effect which never happens to silver under the same circumstances, although silver is a much more oxidable substance than platinum. The fact is, that potash forms with the oxide of the last-named metal a kind of saline compound, in which the platinum oxide acts as an acid; and hence its formation under the *disposing* influence of the powerful base.

In the remarkable decompositions suffered by various organic bodies when heated in contact with caustic alkali or lime, we have other examples of the same fact. Products are generated which are never formed in the absence of the base; the reaction is invariably less complicated, and its results fewer in number and more definite, than in the event of simple destruction by a graduated heat.

There is yet a still more obscure class of phenomena, called *catalytic*, in which effects are brought about by the mere *presence* of a substance which itself undergoes no perceptible change: the experiment mentioned in the chapter on oxygen, in which that gas is obtained, with the greatest facility, by heating a mixture of potassium chlorate and manganese dioxide, is a case in point. The salt is decomposed at a very far lower temperature than would otherwise be required, and yet the manganese oxide does not appear to undergo any alteration, being found after the experiment in the same state as before. It may, however, undergo a temporary alteration. We know, indeed, that this oxide when in contact with alkalis is capable of taking up an additional proportion of oxygen and forming manganic acid; and it is quite possible that in the reaction just considered it may actually take oxygen from the potassium chlorate, and pass to the state of a higher oxide, which, however, is immediately decomposed, the additional oxygen being evolved, and the dioxide returning to its original state. The same effect in facilitating the decomposition of the chlorate is produced by cupric oxide, ferric oxide, and lead oxide, all of which are known to be susceptible of higher oxidation. The oxides of zinc and magnesium, on the contrary, which do not form higher oxides, are not found to facilitate the decomposition of the chlorate; neither is any such effect produced by mixing the salt with other pulverulent substances, such as pounded glass or pure silica.

The so-called catalytic actions are often mixed up with other effects which are much more intelligible, as the action of finely-divided platinum on certain gaseous mixtures, in which the solid appears to condense the gas upon its greatly extended surface, and thereby to induce combination by bringing the particles within the sphere of their mutual attractions.

Influence of Pressure on Chemical Action.—When a body is decomposed by heat in a confined space, and one or more of the separated elements (ultimate or proximate) is gaseous, the decomposition goes on until the liberated gas or vapour has attained a certain tension, greater or less according to the temperature. So long as this temperature remains constant, no further decomposition takes place, neither does any portion of the separated elements recombine; but if the temperature be raised, decomposition recommences, and goes on till the liberated gas or vapour has attained a certain higher tension, also definite for that particular temperature; if, on the other hand, the temperature be lowered, recomposition takes place, until the tension of the remaining gas is reduced to that which corresponds with the lower temperature. These phenomena, which are closely analogous to those exhibited in the vaporisation of liquids, have been especially studied by Deville and Debray.* Deville designates decomposition under these conditions by the term "Dissociation."

When *calcium carbonate* is heated in an iron tube from which the air has been exhausted by means of a mercury-pump, no decomposition takes place at 300°, and a scarcely perceptible decomposition at 440°; but at 800° (in vapour of cadmium) it becomes very perceptible, and goes on till the tension of the evolved carbon dioxide becomes equivalent to 85 millimeters of mercury; there it stops so long as the temperature remains constant; but on raising the temperature to 1040° (in vapour of zinc) more carbon dioxide is evolved until a tension equivalent to about 520 mm. is attained. If the tension be reduced by working the pump, it is soon restored to its former value by a fresh evolution of carbon dioxide. If, on the other hand, the apparatus be allowed to cool, the carbon dioxide is gradually reabsorbed by the quicklime, and a vacuum is re-established in the apparatus.

Similar phenomena are exhibited in the efflorescence of hydrated salts, and in the decomposition of the compounds of ammonia with metallic chlorides, in closed spaces.

If the decomposed body, as well as one at least of its constituents, is gaseous, it is not possible to obtain an exact measurement of the maximum tension corresponding with the temperature; nevertheless the decomposition is found to take place according to the

* Watts's Dictionary of Chemistry, First Supplement, p. 425.

same general law, ceasing as soon as the liberated gases have obtained a certain tension, which is greater as the temperature is higher.

It has long been known that chemical combination between any two bodies capable of uniting directly, takes place only at and above a certain temperature, and that the combination is broken up at a higher temperature; but it is only in later years that we have become acquainted with the fact that bodies like water begin to decompose at temperatures considerably below that which they produce in the act of combining, and therefore that their combination at that temperature is never complete. Grove showed some years ago that water is resolved into its elements in contact with intensely ignited platinum. This reaction has been more closely studied by Deville, who finds that when vapour of water is passed through a heated platinum tube, decomposition commences at 960°—1000° (about the melting point of silver), but proceeds only to a limited extent; on raising the temperature to 1200°, further decomposition takes place, but again only to a limited amount, ceasing in fact as soon as the liberated oxygen and hydrogen have attained a certain higher tension. The quantity of these gases actually collected in this experiment is, however, very small, the greater portion of them recombining as they pass through the cooler part of the apparatus, till the tension of the remainder is reduced to that which corresponds with the lower temperature.

The recombination of the gases may be prevented to a certain extent by means of an apparatus consisting of a wide tube of glazed earthenware, through the axis of which passes a narrower tube of porous earthenware, the two being tightly fitted by perforated corks provided with gas-delivery tubes, and the whole strongly heated by a furnace. Vapour of water is passed through the inner tube, carbon dioxide through the annular space between the two, and the gases, after passing through the heated tubes, are received over caustic potash-solution. The vapour of water is then decomposed by the heat as before; but the hydrogen, according to the laws of diffusion, passes through the porous earthenware into the surrounding atmosphere of carbon dioxide, being thus separated from the oxygen, which remains in the inner tube, and becomes mixed with carbon dioxide passing through the porous septum in the opposite direction to the hydrogen. As these gases pass through the alkaline water, the carbon dioxide is absorbed, and a mixture of hydrogen and oxygen collects in the receiver. A gram of water passed in the state of vapour through such an apparatus yields about a cubic centimeter of detonating gas.

The retarding influence of pressure is seen also in the action of acids upon zinc, or the electrolysis of water, in sealed tubes. In these cases the elimination of a gas is an essential condition of the change, and this being prevented, the action is retarded. On the other hand, there are numerous reactions which are greatly promoted by increased pressure—those, namely, which depend on the solution

of gases in liquids, or on the prolonged contact of substances which under ordinary pressure would be volatilised by heat.

Relations of Heat to Chemical Affinity.—Whatever may be the real nature of chemical affinity, one most important fact is clearly established with regard to it; namely, that its manifestations are always accompanied by the production or annihilation of heat. Change of composition, or chemical action, and heat are mutually convertible: a given amount of chemical action will give rise to a certain definite amount of heat, which quantity of heat must be directly or indirectly expended, in order to reverse or undo the chemical action that has produced it. The production of heat by chemical action, and the definite quantitative relation between the amount of heat evolved and the quantity of chemical action which takes place, are roughly indicated by the facts of our most familiar experience; thus, for instance, the only practically important method of producing heat artificially consists in changing the elements of wood and coal, together with atmospheric oxygen, into carbon dioxide and water; and every one knows that the heat thus obtainable from a given quantity of coal is limited, and is, at least approximately, always the same. The accurate measurement of the quantity of heat produced by a given amount of chemical action is a problem of very great difficulty; chiefly because chemical changes very seldom take place alone, but are almost always accompanied by physical changes, involving further calorimetric effects, each of which requires to be accurately measured and allowed for, before the effect due to the chemical action can be rightly estimated. Thus the ultimate result has, in most cases, to be deduced from a great number of independent measurements, each liable to a certain amount of error. It is therefore not surprising that the results of various experiments should differ to a comparatively great extent, and that some uncertainty should still exist as to the exact quantity of heat corresponding with even the simplest cases of chemical action.

The experiments are made by enclosing the acting substances in a calorimeter, surrounded by water or mercury, the rise of temperature in which indicates the quantity of heat evolved by the chemical action, after the necessary corrections have been made for the heat absorbed by the containing vessel and the other parts of the apparatus, and for the amount lost by radiation, &c. Combustions in oxygen and chlorine are made in a copper vessel surrounded by water; the heat evolved by the mutual action of liquids or dissolved substances is estimated by means of a smaller calorimeter containing mercury. The construction of these instruments and the methods of observation involve details which are beyond the limits of this work.*

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* See Miller's Chemical Physics, pp. 338 *et seq.*, and Watts's Dictionary of Chemistry, iii. 28, 103.

The following table gives the quantities of heat, expressed in heat-units,* evolved in the combustion of various elements, and of a few compounds, in oxygen, referred: (1) to 1 gram of each substance burned; (2) to 1 gram of oxygen consumed; (3) to 1 atom or molecule (expressed in grams), of the various substances:—

Heat of Combustion of Elementary Substances in Oxygen.

Substance.	Product.	Units of heat evolved. By 1 gram of substance.	By 1 gram of oxygen.	By 1 at. of substance.	Observer.
Hydrogen . .	H_2O	33881	4235	33881	Andrews.
		34462	4308	34462	Favre & Silbermann.
Carbon—					
Wood-charcoal .	CO_2	7900	2962	94800	Andrews.
		8080	3030	96960	Favre & Silbermann.
Gas-retort carbon	,,	8047	3018	96564	,,
Native graphite .	,,	7797	2924	93564	,,
Artificial graphite	,,	7762	2911	93144	,,
Diamond . .	,,	7770	2914	93940	,,
Sulphur—					
Native . .	SO_2	2220	2220	71040	,,
Recently melted .	,,	2260	2260	72320	,,
Flowers . .	,,	2307	2307	73821	Andrews.
Phosphorus—					
(Yellow) . .	P_2O_5	5747	4454	178157	,,
Zinc . . .	ZnO	1330	5390	86450	,,
Iron . . .	Fe_3O_4	1582	4153	88592	,,
Tin . . .	SnO_2	1147	4230	135360	,,
Copper . . .	CuO	603	2394	38304	,,

The following results have been obtained by the complete combustion of partially oxidised substances:—

* The unit of heat here adopted, is the quantity of heat required to raise 1 gram of water from 0° to 1° C.

Substance.	Product.	Units of heat evolved.		Observer.
		By 1 gram of substance.	In the formation of 1 molecule of the ultimate product.	
Carbon monoxide, CO . . .	CO_2	2403	67284	Favre & Silbermann.
		2431	68064	Andrews.
Stannous oxide, SnO .	SnO_2	519	69584	,,
Cuprous oxide, Cu_2O .	CuO	256	18304	,,

The last three substances in this table contain exactly half as much oxygen as the completely oxidised products; and on comparing the amount of heat evolved in the formation of one molecule of stannic or cupric oxide from the corresponding lower oxide, with the quantity produced when a molecule of the same product is formed by the complete oxidation of the metal in one operation, we find that the combination of the second half of the oxygen contained in these bodies evolves sensibly half as much as the combination of the whole quantity. In the formation of carbon dioxide, however, the second half of the oxygen appears to develop more than two-thirds of the total amount of heat: but this result is probably due, in part at least, to the fact that when carbon is burned into carbon dioxide, a considerable but unknown quantity of heat is expended in converting the solid carbon into gas, and thus escapes measurement; while, in carbon monoxide, the carbon already exists in the gaseous form, and therefore no portion of the heat evolved in the combustion of this substance is similarly expended in producing a change of state.

It seems probable, also, that a similar explanation may be given of the inequalities in the quantities of heat produced by the combustion of different varieties of pure carbon and of sulphur—that is to say, that a portion of the heat generated by the combustion of diamond and graphite goes to assimilate their molecular condition to that of wood-charcoal, and that there is an analogous expenditure of heat in the combustion of native sulphur.

The quantities of heat evolved in the combination of chlorine, bromine, and iodine with other elements have been determined by Favre and Silbermann, Andrews, and others; but we must refer to larger works for the results.*

* Watts's Dictionary of Chemistry, iii. 109.

Reactions in Presence of Water.—The thermal effects which may result from the reaction of different substances on one another in presence of water, are more complicated than those resulting from direct combination. In addition to the different specific heats of the reagents and products, and to the different quantities of heat absorbed by them in dissolving, or given out by them in combining with water, the conversion of soluble substances into insoluble ones, as a consequence of the chemical action, or the inverse change of insoluble into soluble bodies, are among the secondary causes to which part of the calorimetric effect may be due in these cases.

When a gas dissolves in water, the heat due to the chemical action is augmented by that due to the liquefaction of the gas; so also when a solid body is dissolved in water, the total thermal effect is due in part to the chemical action taking place between the water and the solid, and in part to the liquefaction of the substance dissolved. In the former case the chemical and physical parts of the phenomena both cause evolution of heat: in the latter case the physical change occasions disappearance of heat, and if this effect is greater than that due to the chemical action, the ultimate effect is the production of cold, and it is this which is generally observed.

Cold produced by Chemical Decomposition.—It is highly probable that the thermal effect of the reversal of a given chemical action is in all cases equal and opposite to the thermal effect of that action itself. A direct consequence of this proposition is that *the separation of any two bodies is attended with the absorption of a quantity of heat equal to that which is evolved in their combination.* The truth of this deduction has been experimentally established in various cases, by Woods,* Joule,† and Favre and Silbermann, by comparing the heat evolved in the electrolysis of dilute sulphuric acid, or solutions of metallic salts, with that which is developed in a thin metallic wire by a current of the same strength: also by comparison of the heat evolved in processes of combination accompanied by simultaneous decomposition, with that evolved when the same combination occurs between free elements.

By determining the heat evolved when different metals were dissolved in water or dilute acid, Woods found that it was less than that which would be produced by the direct oxidation of the same metals, by a quantity equal to that which would be obtained by burning the hydrogen set free, or which was expended in decomposing the water or acid; and, therefore, that when this latter quantity was added to the results, they agreed with the numbers given by experiments of direct oxidation.

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* Phil. Mag. [4] ii. 368; iv. 370. † Ibid. iii. 481.

ELECTRO-CHEMICAL DECOMPOSITION; CHEMISTRY OF THE VOLTAIC PILE.

When a voltaic current of considerable power is made to traverse various compound liquids, a separation of the elements of these liquids ensues: provided that the liquid be capable of conducting the current, its decomposition almost always follows.

The elements are disengaged solely at the limiting surfaces of the liquid, where, according to the common mode of speech, the current enters and leaves the latter, all the intermediate portions appearing perfectly quiescent. In addition, the elements are not separated indifferently and at random at these two surfaces; but, on the contrary, make their appearance with perfect uniformity and constancy at one or the other, according to their chemical character, namely, oxygen, chlorine, iodine, acids, &c., at the surface connected with the *copper*, or *positive* end of the battery; hydrogen, the metals, &c., at the surface in connection with the *zinc*, or *negative* extremity of the arrangement.

The terminations of the battery itself—usually, but by no means necessarily, of metal—are designated poles or *electrodes*,* as by their intervention the liquid to be experimented on is made a part of the circuit. The process of decomposition by the current is called *electrolysis*,† and the liquids which, when thus treated, yield up their elements, are denominated *electrolytes*.

When a pair of platinum plates are plunged into a glass of water to which a few drops of oil of vitriol have been added, and the plates are connected by wires with the extremities of an active battery, oxygen is disengaged at the positive electrode, and hydrogen at the negative, in the proportion of one measure of the former to two of the latter nearly. This experiment has already been described.‡

A solution of hydrochloric acid mixed with a little Saxon blue (indigo), and treated in the same manner, yields hydrogen on the negative side and chlorine on the positive, the indigo there becoming bleached.

Potassium iodide dissolved in water is decomposed in a similar manner: the free iodine at the positive side can be recognised by its brown colour, or by the addition of a little gelatinous starch.

All liquids are not electrolytes; many refuse to conduct, and no decomposition can then occur; alcohol, ether, numerous essential oils, and other products of organic chemistry, besides a few saline inorganic compounds, act in this manner, and completely arrest the current of a powerful battery.

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* From ἤλεκτρον, and ὁδός, a way.

† From ἤλεκτρον, and λύειν, to loose.

‡ Page 164.

One of the most important and indispensable conditions of electrolysis is fluidity; bodies which, when reduced to the liquid state, conduct freely, and as freely suffer decomposition, become absolute insulators to the electricity of the battery when they assume the solid state. Lead chloride offers a good illustration of this fact: when fused in a porcelain crucible, it gives up its elements with the utmost ease, and a galvanometer interposed in the circuit is strongly affected. But when the source of heat is withdrawn, and the salt suffered to solidify, signs of decomposition cease, and at the same moment the magnetic needle reassumes its natural position. In the same manner the thinnest film of ice arrests the current of a powerful voltaic apparatus; but the instant the ice is liquefied, so that water communication is restored between the electrodes, the current again passes, and decomposition occurs. Fusion by heat, and solution in aqueous liquids, answer the purpose equally well.

Generally speaking, compound liquids cannot conduct the electric current without being decomposed; but still there are a few exceptions to this statement, which perhaps are more apparent than real. Thus Hittorf has shown that fused silver sulphide, which was formerly regarded as one of the exceptions, cannot be considered to be so, and Beetz has since proved the same to be the case as regards mercuric iodide and lead fluoride.

The quantity of any given compound liquid which can be decomposed by any given electric battery depends on the resistance of the liquid: the more resistance the less decomposition. Distilled water has only a small power of conduction, and is therefore only slightly decomposed by a battery of 30 to 40 pairs; whilst diluted sulphuric acid is one of the best of fluid conductors, and undergoes rapid decomposition by a small battery.

When a liquid which can be decomposed, and a galvanometer, are included in the circuit of an electric current, if the needle of the galvanometer be deflected, it may be always assumed as certain that a portion of liquid, bearing a proportion to the strength of the current, is decomposed, although it may be impossible in many cases, without special contrivances, to detect the products of the decomposition, on account of their minuteness.

The metallic terminations of the battery, the poles or electrodes, have, in themselves, nothing in the shape of attractive or repulsive power for the elements separated at their surfaces. Finely divided metal suspended in water, or chlorine held in solution in that liquid, shows not the least symptom of a tendency to accumulate around them; a single element is altogether unaffected—directly, at least; separation from previous combination is required, in order that this appearance should be exhibited.

It is necessary to examine the process of electrolysis a little more closely. When a portion of hydrochloric acid, for example, is subjected to decomposition in a glass vessel with parallel sides, chlorine is disengaged at the positive electrode, and hydrogen at the negative: the gases are perfectly pure and unmixed. If, while the

Antimonate, $2K_3SbO_4 = 3K_2O,Sb_2O_5$
Thioantimonate, $2K_3SbS_4 = 3K_2S,Sb_2S_5$.

Selenides.—These compounds are analogous in composition and in many of their properties, to the sulphides, and unite one with the other, forming selenium-salts analogous to the oxygen and sulphur salts. They are prepared by fusing the metals with selenium; by precipitating a solution of a heavy metal with hydrogen selenide, or a dissolved selenide of alkali-metal; by heating selenium with a metallic oxide or carbonate; or by igniting a selenite or selenate with hydrogen or charcoal.

The selenides of the alkali-metals are soluble in water; their solutions are colourless when freshly prepared, but gradually turn red from separation of selenium. The selenides of barium, strontium, and calcium are flesh-coloured, insoluble in pure water, but soluble in aqueous selenhydric acid. The selenides of aluminium, beryllium, magnesium, yttrium, and its allied metals (p. 335), and those of manganese and zinc, are also flesh-coloured and insoluble in water. The other metallic selenides are mostly dark-coloured, exhibit metallic lustre, and are mostly more fusible than the corresponding metals. When they are heated to redness in the air, the selenium burns slowly away with a reddish-blue flame, and an odour of horse-radish. Selenides are less soluble in nitric acid than the pure metals; mercury selenide almost insoluble. Chlorine with the aid of heat converts them into chloride of selenium and metallic chlorides. Heated in gaseous hydrogen chloride, they yield metallic chlorides and hydrogen selenide.

Tellurides are analogous in composition and properties to the sulphides and selenides, but they likewise exhibit some of the characters of metallic alloys. The tellurides of alkali-metal are prepared by heating powdered tellurium with alkaline carbonates mixed with finely divided charcoal, or by passing gaseous hydrogen telluride through solutions of the alkalis. Their solutions have a port-wine colour and deposit tellurium on exposure to the air. The other tellurides may be obtained by fusing the respective metals with tellurium, or by precipitating a metallic solution with hydrogen telluride or a telluride of alkali-metal. The tellurides of gold, silver, and bismuth are found native.

Metals also form definite compounds with nitrogen, phosphorus, silicon, boron, and carbon: but these compounds are comparatively unimportant, excepting the carbonides of iron, which form cast iron and steel.

will separate into their elements 166 parts of potassium iodide, 139 parts of lead chloride, &c. Hence the very important conclusion: *The action of the current is perfectly definite in its nature, producing a fixed and constant amount of decomposition, expressed in each electrolyte by the value of its chemical equivalent.*

From a very extended series of experiments, based on this and other methods of research, Faraday was enabled to draw the general inference that effects of chemical decomposition are always proportionate to the quantity of circulating electricity, and may be taken as an accurate and trustworthy measure of the latter. Guided by this highly important principle, he constructed his *voltameter*, an instrument which has rendered the greatest service to electrical science. This is merely an arrangement by which dilute sulphuric acid is decomposed by the current, the gas evolved being collected and measured. By placing such an instrument in any part of the circuit, the quantity of electric force necessary to produce any given effect can be at once estimated; or, on the other hand, any required amount of the latter can be, as it were, measured out and adjusted to the object in view. The voltameter has received many different forms: one of the most extensively useful is that shown in fig. 137, in which the platinum plates are separated by a very small interval, and the gas is collected in a graduated jar standing on the shelf of the pneumatic trough, the tube of the instrument, which is filled to the neck with dilute sulphuric acid, being passed beneath the jar.

Fig. 137.

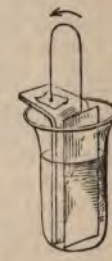
The decomposition produced by the voltaic battery can be effected by the electricity of the common machine, by that developed by magnetic action, and by that of animal origin, though to a much smaller extent. This arises from the very small *quantity* of electricity set in motion by the machine, although its *tension*—that is, power of overcoming obstacles, and passing through imperfect conductors—is exceedingly great. A pair of small wires of zinc and platinum, dipping into a single drop of dilute acid, develops far more electricity, to judge from the chemical effects of such an arrangement, than very many turns of a large plate electrical machine in powerful action. Nevertheless, polar or electrolytic decomposition can be distinctly and satisfactorily effected by the latter, although on a minute scale.

Theory of the Voltaic Battery.—With a knowledge of the principles just laid down, the study of the voltaic battery may be resumed and completed. In the first place, two very different views have been held concerning the source of the electrical disturbance

in that apparatus. Volta himself ascribed it to mere contact of dissimilar metals or other substances conducting electricity,—and, as formerly observed, electric force is actually developed in this way ; but for reasons already given (p. 123) it is much more probable that the chief source of electric power in the battery is the chemical action of the liquid,—always an electrolyte,—on one of the plates, and that the direction of the positive electricity is in all cases from the metal acted upon, through the liquid to the other metal, as is strikingly shown by the experiment already described of plunging a copper and iron couple alternately into dilute sulphuric acid and solution of potassium sulphide (p. 123).

The experiments of Faraday and Daniell have moreover given very great support to the chemical theory, by showing that the contact of dissimilar metals is *not* necessary in order to call into being powerful electrical currents, and that the development of electrical force is not only in some way connected with the chemical action of the liquid of the battery, but is always in direct proportion to the latter. One very beautiful experiment, in which electrolytic decomposition of potassium iodide is performed by a current generated without any contact of dissimilar metals, can be thus made:—A plate of zinc is bent at a right angle, and cleaned by rubbing with sand-paper. A plate of platinum has a wire of the same metal attached to it by careful riveting, and the wire is bent into an arch. A piece of folded filter-paper is wetted with solution of potassium iodide, and placed upon the zinc ; the platinum plate is arranged opposite to the latter, with the end of its wire resting upon the paper ; and then the pair is plunged into a glass of dilute sulphuric, mixed with a few drops of nitric acid. A brown spot of iodine becomes in a moment evident beneath the extremity of the platinum wire—that is, at the positive side of the arrangement.

Fig. 138.



The metals employed in the construction of voltaic batteries are zinc for the active metal, and copper, silver, or, still better, platinum, for the inactive one: the greater the difference of oxidability, the better the arrangement. The liquid is either dilute sulphuric acid, sometimes mixed with a little nitric, or occasionally, where very slow and long-continued action is wanted, salt and water. To obtain the maximum effect of the apparatus with the least expenditure of zinc, that metal must be employed in the pure state, or its surface must be covered by an amalgam, which in its electrical relations closely resembles the pure metal. The zinc is easily brought into this condition by wetting it with dilute sulphuric acid, and then rubbing a little mercury over it, by means of a piece of rag tied to a stick.

The principle of the compound battery is, perhaps, best seen in the crown of cups : by each alternation of zinc, fluid, and copper, the

current is urged forwards with increased energy; its intensity is augmented, but the actual amount of electrical force thrown into the current form is not increased. The quantity, estimated by its decomposing power, is, in fact, determined by that of the smallest and least active pair of plates, the quantity of electricity in every part or section of the circuit being exactly equal. Hence large and small plates, batteries strongly and weakly charged, can never be connected without great loss of power.

When a battery, either simple or compound, constructed with pure or with amalgamated zinc, is charged with dilute sulphuric acid, a number of highly interesting phenomena may be observed. While the circuit remains broken, the zinc is perfectly inactive, no acid is decomposed, no hydrogen liberated; but the moment the connection is completed, torrents of hydrogen arise, not from the zinc, but from the copper or platinum surfaces alone, while the zinc undergoes tranquil and imperceptible oxidation and solution. Thus, exactly the same effects are seen to occur in every active cell of a closed circuit, that are witnessed in a portion of sulphuric acid undergoing electrolysis: oxygen appears at the positive side, with respect to the current, and hydrogen at the negative; but with this difference, that the oxygen, instead of being set free, combines with the zinc. It is, in fact, a real case of electrolysis, and electrolytes alone are available as exciting liquids.

Common zinc is very readily attacked and dissolved by dilute sulphuric acid; and this is usually supposed to arise from the formation of a multitude of little voltaic circles, by the aid of particles of foreign metals or graphite, partially imbedded in the zinc. This gives rise in the battery to what is called local action, by which, in the common forms of apparatus, three-fourths or more of the metal is often consumed, without contributing in the least to the general effect, but, on the contrary, injuring it to some extent. This evil is got rid of by amalgamating the surface.

By careful experiments, in which local action was completely avoided, it has been distinctly proved that the quantity of electricity set in motion by the battery varies exactly with the zinc dissolved. Coupling this fact with that of the definite action of the current, it will be seen that when a perfect battery of this kind is employed to decompose hydrochloric acid, in order to evolve 1 gram of hydrogen from the latter, 32·5 grams of zinc must be dissolved as chloride, and its equivalent quantity of hydrogen disengaged in each active cell of the battery—that is to say, that the electrical force generated by the solution of an equivalent of zinc *in* the battery is capable of effecting the decomposition of an equivalent of hydrochloric acid or any other electrolyte *out* of it.

This is an exceedingly important discovery: it serves to show, in the most striking manner, the intimate nature of the connection between chemical and electrical forces, and their remarkable quantitative or equivalent relations. It almost seems, to use an expression of Faraday, as if a transfer of chemical force took place

through the substance of solid metallic conductors; that chemical actions, called into play in one portion of the circuit, could be made at pleasure to exhibit their effects without loss or diminution in any other.

It is possible however to construct electric circuits containing no electrolytes, but composed entirely of elementary bodies, in which therefore the electric excitement appears to be due to direct combination between elements and to the heat thereby evolved. Messrs. Ayrton and Perry* have constructed such a circuit, capable of producing a current of considerable force, by dipping strips of platinum and magnesium into mercury, and connecting them as in an ordinary voltaic battery. In this case the current appears to be due to the amalgamation of the magnesium. In like manner Exner† has constructed circuits of considerable power, consisting of carbon and a metal (magnesium, aluminium, zinc, &c.) immersed in bromine or in iodine either liquid or solid. In these circuits the positive current goes from the metal through the bromine or iodine to the carbon.

Electro-chemical Theory.—There is an hypothesis, not of recent date, long countenanced and supported by the illustrious Berzelius, which refers all chemical phenomena to electrical forces—which supposes that bodies combine because they are in opposite electrical states; and that even the heat and light accompanying chemical union may be, to a certain extent, accounted for in this manner; that, in short, so far as our present knowledge goes, either electric or chemical action may be assumed as cause or effect: it may be that electricity is merely a form or modification of ordinary chemical affinity; or, on the other hand, that all chemical action is a manifestation of electrical force.

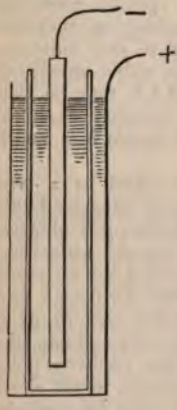
This electro-chemical theory is no longer received as a true explanation of chemical phenomena to the full extent intended by its author. Berzelius, indeed, supposed that the combining tendencies of elements, and their functions in compounds, depend altogether on their electric polarity; and accordingly he divided the elements into two classes, the electro-positive, which like hydrogen and the metals, move towards the negative pole of the battery, as if they were attracted by it, and the electro-negative, which, like oxygen, chlorine and bromine, move towards the positive pole. We are, however, acquainted with a host of phenomena which show that the chemical functions of an element depend upon its position with regard to other elements in a compound, quite as much as upon its individual character. Thus chlorine, the very type of an electro-negative element, can be substituted for hydrogen, one of the most positive of the elements, in a large number of compounds,

* Proceedings of the Royal Society, xxvii. 222.
† Wiedermann's Annalen, xv. 412.

yielding new products, which exhibit the closest analogy in composition and properties to the compounds from which they are derived. It is impossible, therefore, to admit that the chemical functions of bodies are determined exclusively by their electrical relations. Still it is true in a general way that those elements which differ most strongly in their electrical characters, chlorine and potassium, for example, are likewise those which combine together with the greatest energy; and the division of bodies into electro-positive and electro-negative is therefore retained; the former are also called acid or chlorous, and the latter basylous or zincous.

Constant Batteries.—In all the older forms of the voltaic battery, such as those described on pages 124 and 125, the power rapidly decreases, so that after a short time, scarcely the tenth part of the original action remains. This loss of power depends, partly on the gradual change of the sulphuric acid into zinc sulphate, but still more on the coating of hydrogen, and, at a later stage, on the precipitation of metallic zinc on the copper plates. It is self-evident that if the copper plate in the liquid became covered with zinc, it would act electrically like a zinc plate.

Fig. 139.



To prevent this alteration of the negative plate, and consequent loss of electric power, it is necessary either to remove the hydrogen as fast as it accumulates, or to prevent its evolution altogether, and for this purpose various forms of battery have been devised.

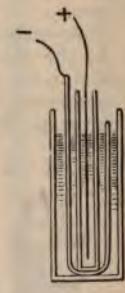
Daniell's Battery.—In this form of battery (fig. 139) each cell consists of a copper cylinder within which is placed a hollow cylinder of unglazed earthenware, animal membrane, or parchment-paper, in the axis of which is placed a rod of amalgamated zinc. This inner cylinder is filled with a mixture of 1 part by measure of oil of vitriol and 8 of water, and the exterior space with the same liquid saturated with copper sulphate. A sort of little colander is fitted to the top of the cell, in which crystals of the copper sulphate are placed, so that the strength of the solution may remain unimpaired. When a communication is made by a wire between the rod and the copper cylinder, a strong current is produced, the power of which may be increased to any extent by connecting a sufficient number of such cells into a series, on the principle of the crown of cups, the copper of the first being attached to the zinc of the second. Ten such alternations constitute a very powerful apparatus, which has the great advantage of retaining its energy undiminished for a long time.

By this arrangement of the voltaic battery, the accumulation of

hydrogen and deposition of zinc on the surface of the copper plate is altogether avoided ; the zinc in the porous cell, whilst it dissolves in the sulphuric acid, decomposes it, but does not liberate any hydrogen ; for by the progress of the decomposition (see p. 315), up to the boundary of the copper solution, the hydrogen takes the place of the copper, and thus ultimately the copper is precipitated on the copper plate. The copper plate therefore remains in its original state, so long as a sufficient quantity of copper sulphate is present in the solution.

Grove's Battery.—This form of battery is capable of producing a far greater degree of power than that last mentioned, and hence it has become one of the most important means of promoting electrical science in the present day. One of the cells is represented in fig. 140. The zinc plate is bent round, so as to present a double surface, and is well amalgamated : within it stands a thin flat cell of porous earthenware, filled with strong nitric acid, and the whole is immersed in a mixture of 1 part by measure of oil of vitriol and 6 of water, contained either in one of the cells of Woollaston's trough, or in a separate cell of glazed porcelain, made for the purpose. The arrangement is completed by a strip of platinum foil, which dips into the nitric acid. In this arrangement there is no accumulation of hydrogen on the negative plate, and consequently no polarisation : for the hydrogen, in passing through the nitric acid in its progress towards the platinum plate, decomposes the nitric acid, and is itself oxidised to water, while fumes of nitrogen peroxide are given off. This gas does not, however, form bubbles on the platinum plate, as it is very easily soluble in nitric acid ; neither does it, like hydrogen, tend to set up a current in the contrary direction. With ten such pairs, experiments of decomposition, ignition of wires, the light between charcoal points, &c., can be exhibited with great brilliancy, while the battery itself is very compact and portable, and, to a great extent, constant in its action. The zinc, as in the case of Daniell's battery, is consumed only while the current passes, so that the apparatus may be arranged an hour or two before it is required for use, which is often a matter of great convenience ; and local action from the precipitation of copper on the zinc is avoided.

Fig. 140.



Professor Bunsen has modified the Grove battery by substituting for the platinum dense charcoal or coke, which is an excellent conductor of electricity. By this alteration, at a very small expense, a battery may be made nearly as powerful and useful as that of Grove.

Fig. 141 shows the form of the round carbon cylinder which is used in these cells. It is hollowed so as to receive a porous earthenware cell, in which a round plate of zinc is placed. The upper

Potassium Chlorate, $KClO_3 = ClO_2(OK)$.—The theory of the production of chloric acid by the action of chlorine gas on a solution of caustic potash, has been already explained (p. 181). Chlorine gas is conducted by a wide tube into a strong and warm solution of potassium carbonate, until absorption of the gas ceases; and the liquid is, if necessary, evaporated, and then left to cool, in order that the slightly soluble chlorate may crystallise out. The mother-liquor affords a second crop of crystals, but they are much more contaminated with potassium chloride. It may be purified by one or two re-crystallisations.

Potassium chlorate is soluble in about 20 parts of cold and 2 of boiling water: the crystals are anhydrous, flat, and tabular; in taste it somewhat resembles nitre. When heated it gives off the whole of its oxygen as gas and leaves potassium chloride. By arresting the decomposition when the evolution of gas begins to slacken, and redissolving the salt, potassium perchlorate and chloride may be obtained.

This salt deflagrates violently with combustible matter, explosion often occurring by friction or blows. When about 1 grain-weight of chlorate and an equal quantity of sulphur are rubbed in a mortar, the mixture explodes with a loud report: hence it cannot be used in the preparation of gunpowder instead of the nitrate. Potassium chlorate is now a large article of commerce, being employed, together with phosphorus, in making instantaneous-light matches.

Potassium Perchlorate, $KClO_4 = ClO_3(OK)$.—This salt has been already noticed under the head of perchloric acid. It is best prepared by projecting powdered potassium chlorate into warm nitric acid, when the chloric acid is resolved into perchloric acid, chlorine and oxygen. The salt is separated from the nitrate by crystallisation. Potassium perchlorate is a very slightly soluble salt: it requires 55 parts of cold water, but is more freely taken up at a boiling heat. The crystals are small, and have the figure of an octohedron with square base. It is decomposed by heat in the same manner as the chlorate.

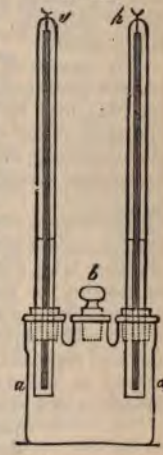
Potassium Bromate, $KBrO_3$, is obtained by passing chlorine into a warm solution of potassium bromide and caustic potash: $KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O$. The solution on cooling deposits part of the bromate, and the rest may be separated by precipitation with alcohol. It crystallises in six-sided tables or prisms, moderately soluble in hot, very slightly in cold water.

Potassium Iodate, KIO_3, is prepared by passing chlorine into cold water containing iodine in suspension till the whole is dissolved, then adding the calculated quantity of potassium chlorate and warming: $ICl + KClO_3 = Cl_2 + KIO_3$. It forms small cubic crystals, and requires a much stronger heat to decompose it than the chlorate. It unites with iodic acid, forming the salts KIO_3,HIO_3

silver chloride. As the zinc dissolves, silver is continually deposited on the wire, just as copper is deposited in the Daniell cells. The electromotive force of this battery is about equal to that of Daniell's. A battery of 11,000 of these cells gives a spark not quite a quarter of an inch long.

Secondary Batteries.—Storage of Electric Currents.—If a voltameter which has been used for some time for decomposing acidulated water—so that the platinum electrodes have become coated with the electrolytic gases, the anode with oxygen and the cathode with hydrogen—be disconnected from the battery, and its wires then connected with a galvanometer, a current will be produced in the direction opposite to that of the original current,—that is to say, the positive electricity will proceed from the hydrogen plate through the liquid to the oxygen plate, the film of hydrogen, in fact, being oxidised by the acid liquid, and acting just like the zinc plate of an ordinary voltaic couple. The same effect is produced by a pair of platinum plates immersed in hydrogen and oxygen gases respectively, and plunged into acidulated water, as in Grove's gas-battery (fig. 143). The gases condense on the surfaces of the two plates, or are occluded by them, the plate immersed in the hydrogen then acting like the zinc of an ordinary voltaic battery, and producing a current the direction of which is indicated by the arrows in the figure.

Fig. 143.



If the electrodes of a voltameter, after having been charged by the battery as above described, be left at rest for some time, and then connected through the medium of a galvanometer or otherwise, a reverse current will be produced, and in this way the power generated by a voltaic battery or other source of electricity may be stored up for use when required.

A more abundant storage of electric power may however be obtained by the electrolysis of a lead-salt, whereby, as already observed (p. 316), metallic lead is deposited on the cathode and dioxide of lead, PbO_2, on the anode; and when the plates thus coated are immersed in dilute sulphuric acid, the metallic lead becomes oxidised and the dioxide reduced, and a current is thereby developed, the positive electricity proceeding from the former to the latter, *i.e.*, in a direction opposite to that of the original battery current. If the plates are left unconnected, they may remain in the acid liquid for days without undergoing any change, or showing any signs of electric charge; but on connecting them by a wire, a current is immediately produced in the direction just indicated. Such is the principle of the secondary battery, invented by Gustav Planté, the plates of which consist of two pieces of sheet lead, rolled up

together in cylindrical form, but not in metallic contact with each other. Its power may be greatly increased, as recommended by Faure, by covering the lead plates with a coating of minium or red lead, an oxide intermediate between PbO and PbO_2. On passing a current through the cell, the red lead is peroxidised at the positive, and reduced at the negative electrode, first to a lower oxide, then to metallic lead. In this way a greater thickness of the working substance is obtained, and the time of charging is much shortened.

H. Sutton* has devised a storage battery composed of amalgamated lead plates and plates of copper immersed in solution of copper sulphate. On connecting the lead plates with the positive pole of a battery, the lead becomes peroxidised, metallic copper is deposited on the copper plate, and sulphuric acid remains in solution. The battery is thus charged, and during its discharge the peroxide of lead is reduced, and the copper is oxidised and dissolved, reproducing copper sulphate. This form of battery is said to be very powerful and constant.

By means of these storage-batteries the power of an electric current generated in any way, by a dynamo-machine, for example (p. 132), may be stored up and transported to any place at which it is required for use, as for working a railway, driving machinery, electroplating, electric lighting, &c. Faure's batteries are made with flat plates, arranged in a rectangular trough.

Electrotype.—Within the last forty years several very beautiful and successful applications of voltaic electricity have been made of which a brief notice must suffice. Spencer and Jacobi employed it in copying, or rather in multiplying, engraved plates and medals, by depositing upon their surfaces a thin coating of metallic copper, which when separated from the original, exhibits, in reverse, a most faithful representation of the latter. By using this in its turn as a mould or matrix, an absolutely perfect *fac-simile* of the plate or medal is obtained. In the former case, the impressions taken on paper are quite undistinguishable from those directly derived from the work of the artist; and as there is no limit to the number of *electrotype* plates which can be thus produced, engravings of the most beautiful description may be multiplied indefinitely. The copper is very tough, and bears the action of the press perfectly well.

Fig. 144.

The apparatus used in this and many similar processes is of the simplest kind. A trough or cell of wood is divided by a porous diaphragm, made of a very thin piece of sycamore, into two parts; dilute sulphuric acid is put on one side, and a saturated solution of copper sulphate, sometimes mixed with a little acid, on the other. A plate of zinc is soldered to

* Chemical News, xliv. 298.

a wire or strip of copper, the other end of which is secured by similar means to the engraved copper plate. The latter is then immersed in the solution of sulphate, and the zinc in the acid. To prevent deposition of copper on the back of the copper plate, that portion is covered with varnish. For medals and small works, a porous earthenware cell, placed in a jelly-jar, may be used.

Other metals may be precipitated in the same manner, in a smooth and compact form, by the use of certain precautions which have been gathered by experience. Electro-gilding and plating are now carried on very largely and in great perfection by Messrs. Elkington and others. Even non-conducting bodies, as sealing-wax and plaster of Paris, may be coated with metal; it is only necessary, as shown by the late Mr. Robert Murray, to rub over them the thinnest possible film of plumbago. Seals may thus be copied in a very few hours with unerring truth.

The common but very pleasing experiment of the *lead-tree* is greatly dependent on electro-chemical action. When a piece of zinc is suspended in a solution of lead acetate, the first effect is the decomposition of a portion of the latter, and the deposition of metallic lead upon the surface of the zinc; it is simply a displacement of a metal by a more oxidable one. The change does not, however, stop here; metallic lead is still deposited in large and beautiful plates upon that first thrown down, until the solution becomes exhausted, or the zinc entirely disappears. The first portions of lead form with the zinc a voltaic arrangement of sufficient power to decompose the salt: under the peculiar circumstances in which the latter is placed, the metal is precipitated upon the negative portion —that is, the lead—while the oxygen and acid are taken up by the zinc.

Fig. 145.

Becquerel, several years ago, published an exceedingly interesting account of certain experiments in which crystallised metals, oxides, and other insoluble substances had been produced by the slow and continuous action of feeble electrical currents, kept up for months, or even years. These products exactly resemble natural minerals: and, indeed, the experiments throw great light on the formation of the latter within the earth.*

Heat developed by the Electric Current.—All parts of the electric circuit, the plates, the liquid in the cells of the battery, the conducting wires, and any electrolytes undergoing decomposition, all become heated during the passage of the current. The rise of temperature in any part of the circuit depends partly on the strength of the current, partly on its resistance, those bodies which offer the

* Traité de l'Electricité et du Magnétisme, iii. 239.

greatest resistance, or are the worst conductors, being most strongly heated by a current of given strength. Thus, when a thick and a thin wire of the same metal are included in the same circuit, the latter becomes more strongly heated, and a platinum wire is much more strongly heated than a silver or copper wire of the same thickness.

By exact experiments it has been found that both in metallic wires and in liquids traversed by an electric current, the evolution of heat is directly proportional—1st, *to the resistance;* 2nd, *to the strength of the current.* Joule has* also shown that the evolution of heat in each couple of the voltaic battery is subject to the same law, which, therefore, holds good in every part of the circuit, including the battery.

The strength of an electric current may be measured by the quantity of detonating gas (2 vols. H to 1 vol. O) which it can evolve from acidulated water in a given time, the *unit of current strength being the current which eliminates one cubic centimeter of detonating gas at* 0° C. and 760 mm. *barometric pressure in a minute.*† Now Lenz has shown that when a current of this strength passes through a wire whose resistance is equal to that of a copper wire 1 meter long and 1 millimeter in diameter, it develops a quantity of heat sufficient to raise the temperature of 1 gram of water from 0° to 1° C. in $5\frac{3}{4}$ minutes; and assuming as the unit of heat the quantity required to raise the temperature of 1 gram of water from 0° to 1° C., the law may be thus expressed—

A current of the unit of strength passing through a conductor which exerts the unit of resistance, develops therein 1·057 *heat-unit in an hour, or* 0·0176 *heat-unit in a minute.*

With a current of given strength, the sum of the quantities of heat evolved in the battery and in the metallic conductor joining its poles, is constant, the heat actually developed in the one part or the other varying according to the thickness of the metallic conductor. This was first shown by De la Rive, and has been confirmed by Favre.‡ De la Rive made use of a couple consisting of platinum and distilled zinc or cadmium, excited by pure and very strong nitric acid, the two metals being united by a platinum wire, more or less thick, which was plunged into the same quantity of strong nitric acid contained in a capsule, similar to that which held the voltaic couple. By observing the temperatures in the two vessels with delicate thermometers, the sum of these temperatures was found to be constant, the one or the other being greater according to the thickness of the connecting wire.

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* Phil. Mag. [3] xix. 210.

† Respecting the units of Current-strength and Resistance now adopted by practical electricians, see Thompson's "Elementary Lessons in Electricity and Magnetism" (pp. 378—380).

‡ Ann. Ch. Phys. [3] xl. 393.

Favre,* by means of a calorimeter, similar to that which he used in his experiments on the development of heat by chemical action, has shown that, in a pair of zinc and platinum plates, excited by dilute sulphuric acid and connected by platinum wires of various length and thickness,—for every 32·5 grams of zinc dissolved, a quantity of heat is developed in the entire circuit, equal to 18,173 heat-units, but variously distributed between the battery-cell and the wire, according to the thickness of the latter. Now this quantity of heat is nearly the same as that which is evolved in the simple solution of 32·5 grams of zinc in dilute sulphuric acid, without the formation of a voltaic circuit, viz., 18,444 units. Hence Favre concludes that the heat developed by the resistance of a metallic or other conductor connecting the poles of the battery, is simply borrowed from the total quantity of heat evolved by the chemical action taking place in the battery, and is rigorously complementary to that which remains in the cells of the battery, the heat evolved in the entire circuit being the exact equivalent of the chemical action which takes place. If any external work is performed by the current, such as electrolysis, or mechanical work, as by an electro-magnetic engine, the heat evolved in the circuit is diminished by the heat-equivalent of the decomposition or mechanical work done.

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* Comptes Rendus, xlv. 56.

CHEMISTRY OF THE METALS.

THE metals constitute the second and larger group of elementary bodies. A great number of them are of very rare occurrence, being found only in a few scarce minerals; others are more abundant, and some few are almost universally diffused throughout the globe. Some of these bodies are of most importance when in the metallic state; others, when in combination, chiefly as oxides, the metals themselves being almost unknown. Many are used in medicine and in the arts, and are essentially connected with the progress of civilisation.

The number of metals at present known is fifty-three.

Physical Properties.—One of the most remarkable and striking characters possessed by the metals is their peculiar lustre: this is so characteristic, that the expression *metallic lustre* has passed into common speech. This property is no doubt connected with the great degree of opacity which the metals present in every instance, the thinnest leaves or plates of these bodies, and the edges of crystalline laminæ, completely arresting the passage of light. An exception to the rule is usually made in favour of gold-leaf, which, when held up to day-light, exhibits a greenish, and in some cases a purple colour, as if it were really endued with a certain degree of translucency: the metallic film is, however, generally so imperfect that it is somewhat difficult to say whether the observed effect may not be in some measure due to multitudes of little holes, many of which are visible to the naked eye; but Faraday's experiments have established the translucency of gold beyond all doubt.

In point of *colour*, the metals present a certain degree of uniformity: with two exceptions—viz., copper, which is red, and gold, which is yellow—all these bodies are included between the pure white of silver and the bluish-grey tint of lead: bismuth, it is true, has a pinkish colour, and calcium and strontium a yellowish tint, but these tints are very feeble.

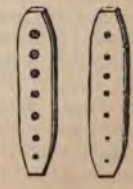
The differences of *density* are very wide, passing from lithium, potassium, and sodium, which are lighter than water, to platinum, which is more than twenty-one times heavier than an equal bulk of that liquid.

	Density.	Temp.		Density.	Temp.
Osmium .	22·48		Cadmium .	8·66	
Iridium .	22·40		Molybdenum	8·63	
Platinum .	21·50		Cobalt . .	8·51	
Gold . .	19·265	13°	Manganese .	8·02	
Uranium .	18·40	0°	Iron . .	7·79	
Tungsten .	18·30		Tin . .	7·29	13°
Mercury .	13·60		Zinc . .	6·915	
Rhodium .	12·1		Antimony .	6·72	14°
Thallium .	11·8		Aluminium .	2·67	
Palladium .	11·4	22·5°	Magnesium .	1·74	5°
Lead . .	11·37	14°	Calcium .	1·58	
Silver . .	10·47	13°	Rubidium .	1·52	
Bismuth .	9·82	12°	Sodium .	0·97	10°
Copper .	8·95		Potassium .	0·865	
Nickel . .	8·82		Lithium .	6·59	

The property of *malleability*, or power of extension under the hammer, or between the rollers of the flatting-mill, is possessed by certain of the metals to a very great extent. Gold-leaf is a remarkable example of the tenuity to which a malleable metal may be brought by suitable means. The gilding on silver wire used in the manufacture of gold lace is even thinner, and yet presents an unbroken surface. Silver may be beaten out very thin—copper also, but to an inferior extent; tin and platinum are easily rolled out into foil; iron, palladium, lead, nickel, cadmium, and metals of the alkalis, and mercury when solidified, are also malleable. Zinc may be placed midway between the malleable and brittle division; then perhaps bismuth: and, lastly, such metals as antimony, which are altogether destitute of malleability.

The density of malleable metals is usually very sensibly increased by pressure or blows, and the metals themselves are rendered much harder, with a tendency to brittleness. This condition is destroyed and the former soft state restored by the operation of *annealing*, which consists in heating the metal to redness out of contact with air (if it will bear that temperature without fusion), and cooling it, quickly or slowly according to the circumstances of the case. After this operation, it is found to possess its original density.

Fig. 146.



Ductility is a property distinct from the last, inasmuch as it involves the principle of tenacity, or power of resisting tension. The art of wire-drawing is one of great antiquity; it consists in drawing rods of metal through a succession of trumpet-shaped holes in a steel plate, each being a little smaller

than its predecessor, until the requisite degree of fineness is attained. The metal often becomes very hard and rigid in this process, and is then liable to break: this is remedied by annealing. The order of tenacity among the metals susceptible of being easily drawn into wire is the following: it is determined by observing the weights required to break asunder wires drawn through the same orifice of the plate:—

Iron.	Gold.
Copper.	Zinc.
Platinum.	Tin.
Silver.	Lead.

Metals differ as much in *fusibility* as in density. The following table will give an idea of their relations to heat:—

		Melting points.
Fusible below a red heat.	Mercury	− 39·44°
	Gallium	+ 30
	Rubidium	+ 38·5
	Potassium	62·5
	Sodium	95·6
	Lithium	180
	Tin	235
	Bismuth	270
	Thallium	294
	Cadmium	315
	Lead	334
	Zinc	423
	Antimony	425
Infusible below a red heat.	Silver	1000
	Copper	1090
	Gold	1102
	Cast iron	1530
	Pure iron, Nickel, Cobalt, Manganese, Palladium,	Highest heat of Forge.
	Molybdenum, Uranium, Tungsten, Chromium,	Agglomerate, but do not melt in the forge.
	Titanium, Cerium, Osmium, Iridium, Rhodium, Platinum, Tantalum,	Infusible in ordinary blast-furnaces; fusible by oxy-hydrogen blow-pipe.

Some metals acquire a pasty or adhesive state before becoming fluid: this is the case with iron and platinum, and with the metals of the alkalis. It is this peculiarity which confers the very valuable property of welding, by which pieces of iron and steel are united without solder, and the finely-divided metallic sponge of platinum is converted into a solid and compact bar.

Some metals are *volatile*, and this character would perhaps be exhibited by all, could sufficiently high temperatures be obtained. Mercury boils and distils below a red heat; potassium, sodium, zinc, magnesium, and calcium rise in vapour when heated to bright redness.

CHEMICAL RELATIONS OF THE METALS.

METALLIC combinations are of two kinds—namely, those formed by the union of metals among themselves, which are called *alloys*, or, where mercury is concerned, *amalgams*, and those generated by combination with the non-metallic elements, as oxides, chlorides, sulphides, &c. In this latter case, the metallic characters are almost invariably lost.

Alloys.—Most metals are probably, to some extent, capable of existing in a state of combination with each other in definite proportions; but it is difficult to obtain these compounds in the separate state, since they dissolve in all proportions in the melted metals, and do not generally differ so widely in their melting points from the metals they may be mixed with, as to be separated by crystallisation in a definite form. Exceptions to this rule are met with in the cooling of argentiferous lead, and in the crystallisation of brass and of gun-metal.

The chemical force capable of being exerted between different metals is for the most part very feeble, and the consequent state of combination is therefore very easily disturbed by the influence of other forces. The stability of such metallic compounds is, however, greater in proportion to the general chemical dissimilarity of the metals they contain. But in all cases of combination between metals, the alteration of physical characters, which is the distinctive feature of chemical combination, does not take place to any great extent. The most unquestionable compounds of metals with metals are still metallic in their general physical characters, and there is no such transmutation of the individuality of their constituents as takes place in the combination of a metal with oxygen, sulphur, chlorine, &c. The alteration of characters in alloys is generally limited to the colour, degree of hardness, tenacity, &c., and it is only when the constituent metals are capable of assuming opposite chemical relations that these compounds are distinguished by great brittleness. The formation of actual chemical compounds, in some cases, when

two metals are melted together, is indicated by several phenomena, viz., the evolution of heat, as in the case of platinum and tin, copper and zinc, &c.

The density of alloys differs from that of mere mixtures of the metals. In the solidification of alloys, the temperature does not always fall uniformly, but often remains stationary at particular degrees, which may be regarded as the solidifying points of the compounds then crystallising. Tin and lead melted together in any proportions always form a compound which solidifies at 187°. The melting point of an alloy is often very different from the point of solidification, and it is generally lower than the mean melting point of the constituent metals.

But though metals may combine when melted together, it is doubtful whether they remain combined after the solidification of the mass, and the wide difference between the melting and solidifying points of certain alloys appear to indicate that the existence of these compounds is limited to a certain range of temperature. Matthiessen* regards it as probable that the condition of an alloy of two metals in the liquid state may be either that of—1. A solution of one metal in another; 2. Chemical combination; 3. Mechanical mixture: or, 4. A solution or mixture of two or all of the above; and that similar differences may exist as to its condition in the solid state.

The chemical action of reagents upon alloys is sometimes very different from their action upon metals in the separate state: thus, platinum alloyed with silver is readily dissolved by nitric acid, but is not affected by that acid when unalloyed. On the contrary, silver, which in the separate state is readily dissolved by nitric acid, is not dissolved by it when alloyed with gold in proportions much less than one-fourth of the alloy by weight.

Compounds of Metals with Metalloids—Classification of Metals.

A classification of the metals according to their quantivalence or atomicity is given in the table on page 290. There are, however, several metals, especially among those of rare occurrence, whose position in the series is by no means definitely fixed; and partly on this account, but chiefly because metals of equal quantivalence or combining capacity do not, as a rule, resemble one another in their physical and chemical characters so closely as non-metallic elements of equal combining capacity (*e.g.*, Cl, Br, I, F, and O, S, Se, Te, &c.), it is found advisable, in describing the metals, to classify them according to their general agreement in physical and chemical properties rather than according to their quantivalence.

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* British Association Reports, 1863, p. 97.

The following arrangement based upon this principle does not, however, deviate greatly from the order of quantivalence:—

1. METALS OF THE ALKALIS:—
   Potassium—Sodium—Lithium—Rubidium—Cæsium.

2. METALS OF THE ALKALINE EARTHS:—
   Calcium—Strontium—Barium.

3. MAGNESIUM GROUP:—
   Beryllium—Magnesium—Zinc—Cadmium.

4. LEAD GROUP:—
   Lead—Thallium.

5. COPPER GROUP:—
   Copper—Silver—Mercury.

6. YTTRIUM GROUP:—
   Yttrium—Erbium—Terbium—Ytterbium—Scandium—Decipium—Lanthanum—Cerium—Didymium.

7. ALUMINIUM GROUP:—
   Aluminium—Indium—Gallium.

8. IRON GROUP:—
   Manganese—Iron—Cobalt—Nickel.

9. CHROMIUM GROUP:—
   Chromium—Molybdenum—Tungsten—Uranium.

10. TIN GROUP:—
    Tin—Titanium—Zirconium—Thorium.

11. ANTIMONY GROUP:—
    Vanadium—Antimony—Bismuth—Tantalum—Niobium.

12. PLATINUM GROUP:—
    Gold—Platinum—Palladium—Rhodium—Iridium—Ruthenium—Osmium.

The degrees of quantivalence or combining capacity of the metals in these several groups are for the most part less easy to determine than those of the non-metallic elements. All the latter unite with hydrogen, forming volatile compounds, the vapour-densities of which are easily determined, and afford trustworthy data for fixing the molecular weight and constitution of these compounds (p. 134). Hydrogen silicide, for example, has a vapour-density of 16: consequently its molecular weight is 32 (p. 278), and, as

analysis shows the compound to contain 7 pts. by weight of silicon to 1 pt. of hydrogen, its molecule must contain 28 pts. Si and 4H, and its molecular formula must be SiH_4, showing that silicon is a tetrad. But with the metals this mode of proceeding is not available: for only one of them, viz., antimony, forms a volatile compound with hydrogen; and if we endeavour to fix the quantivalence of a metal by its mode of combination with chlorine or other univalent element, we find that the results are not always accordant. With regard to some of the groups, indeed, this mode of determining the quantivalence of a metal appears to be satisfactory. Thus the metals of the first, second, third, sixth, tenth, and eleventh groups form chlorides related to one another as represented by the formulæ :—

1.	2.	3.	6.	10.	11.
RCl	RCl_2	RCl_2	RCl_3	RCl_4	RCl_5,

but in the chromium group (9) anomalies present themselves; thus molybdenum and tungsten form pentachlorides, whence it might be inferred that they are pentads: but tungsten also forms a hexchloride, and both these metals, in their oxygen-compounds, exhibit so marked an analogy to sulphur, that they must be regarded as hexads.

Moreover, we have no means of ensuring that the formulæ assigned to these several chlorides actually represent their molecules; for the only trustworthy method of determining the weight of a molecule is by means of its vapour-density, and in the case of the greater number of metallic chlorides (also bromides and iodides), this determination cannot be made, on account of the very high temperatures required to volatilise them.

In many cases indeed it seems probable that the molecular constitution of metallic chlorides, bromides, &c., should be represented, not by formulæ containing single atoms of the respective metals, like those above given, but by multiples thereof,—potassium chloride, for example, by the double formula K_2Cl_2 or Cl—K—K—Cl, into which the metal enters as a dyad, or even by some higher multiple, for example by

$$K_4Cl_4 = \begin{array}{c} Cl—K—K—Cl \\ \quad | \quad | \\ Cl—K—K—Cl \end{array} \quad \text{or} \quad \begin{array}{c} Cl—K—K—Cl \\ \quad \| \quad \| \\ Cl—K—K—Cl \end{array}, \text{ &c.,}$$

the potassium appearing as a triad or a tetrad, according to the manner in which we may imagine its atoms to be linked together. For, since both potassium and chlorine are easily volatile bodies, the chloride, if correctly represented by the simpler formula K.Cl, might be expected to volatilise at a comparatively low temperature, lower, for example, than those required to volatilise the more complex and heavier molecules $HgCl_2$ and $SbCl_3$, whereas it actually

requires a strong red heat to convert it into vapour; and similar remarks might be made with regard to many other haloïd salts of the metals. In stating, therefore, that potassium chloride is represented by the formula KCl, and calcium chloride by $CaCl_2$, all that we mean to say is that for every atom of metal in these compounds, the first contains one atom of chlorine, and the second two atoms; and in this sense—whatever may be the number of atoms contained in the molecule—potassium is certainly univalent, or equivalent to one atom of hydrogen, and calcium bivalent, or equivalent to two atoms of hydrogen.

The metals of the alkalis and alkaline earths, on account of their inferior density, are often called light metals; the others, heavy metals.

Metallic Chlorides.—All metals combine with chlorine, and most of them in several proportions, as above indicated, forming compounds which may be regarded as derived from one or more molecules of hydrochloric acid, by substitution of a metal for an equivalent quantity of hydrogen; thus:—

From	HCl	are derived	monochlorides	like	KCl
„	H_2Cl_2	„	dichlorides	„	$BaCl_2$
„	H_3Cl_3	„	trichlorides	„	$AuCl_3$
„	H_4Cl_4	„	tetrachlorides	„	$SnCl_4$, &c., &c.

Hydrochloric acid may, in fact, be regarded as the type of chlorides in general.

Several chlorides occur as natural products. Sodium chloride, or common salt, occurs in enormous quantities, both in the solid state as rock-salt, and dissolved in sea-water, and in the water of rivers and springs. Potassium chloride occurs in the same forms, but in smaller quantity; the chlorides of lithium, cæsium, rubidium, and thallium also occur in small quantities in certain spring waters. Mercurous chloride, Hg_2Cl_2, and silver chloride, AgCl, occur as natural minerals.

1. Chlorides are generally prepared by one or other of the following processes: (1.) By acting upon the metal with chlorine gas. Antimony pentachloride and copper dichloride are examples of chlorides sometimes produced in this manner. The chlorides of gold and platinum are usually prepared by acting upon the metals with nascent chlorine, developed by a mixture of hydrochloric and nitric acids (p. 215). Sometimes, on the other hand, the metal is in the nascent state, as when titanic chloride is formed by passing a current of chlorine over a heated mixture of charcoal and titanic oxide. The chlorides of aluminium and chromium may be obtained by similar processes.

2. Chlorine gas, by its action upon metallic oxides, drives out

the oxygen, and unites with the respective metals to form chlorides. This reaction sometimes takes place at ordinary temperatures, as is the case with silver oxide; sometimes only at a red heat, as is the case with the oxides of the alkali-metals and alkaline earth-metals. The hydroxides and carbonates of these last metals, when dissolved or suspended in hot water and treated with excess of chlorine, are converted, chiefly into chlorides, partly into chlorates.

3. Many metallic chlorides are prepared by acting upon the metals with hydrochloric acid. Zinc, cadmium, iron, nickel, cobalt, and tin dissolve readily in hydrochloric acid, with liberation of hydrogen; copper only in the strong boiling acid; silver, mercury, palladium, platinum and gold, not at all. Sometimes the metal is substituted, not for hydrogen, but for some other metal. Stannous chloride, for instance, is frequently made by distilling metallic tin with mercuric chloride; thus: $HgCl_2 + Sn = SnCl_2 + Hg$.

4. By dissolving a metallic oxide, hydroxide, or carbonate in hydrochloric acid.

All monochlorides and dichlorides are soluble in water, excepting silver chloride, AgCl, and mercurous chloride, Hg_2Cl_2; lead chloride, $PbCl_2$, is sparingly soluble; these three chlorides are easily formed by precipitation. Many metallic chlorides dissolve also in alcohol and in ether.

Most monochlorides, dichlorides, and trichlorides volatilise at high temperatures without decomposition; the higher chlorides when heated give off part of their chlorine. Some chlorides which resist the action of heat alone are decomposed by ignition in the air, yielding metallic oxides and free chlorine: this is the case with the dichlorides of iron and manganese; but most dichlorides remain undecomposed, even in this case. All metallic chlorides, excepting those of the alkali-metals and earth-metals, are decomposed at a red heat by hydrogen gas, with formation of hydrochloric acid: in this way metallic iron may be obtained in fine cubical crystals. Silver chloride, placed in contact with metallic zinc or iron, under dilute sulphuric or hydrochloric acid, is reduced to the metallic state by the nascent hydrogen.

Sulphuric, phosphoric, boric, and arsenic acids decompose most metallic chlorides, sometimes at ordinary, sometimes at higher temperatures. All metallic chlorides, heated with lead dioxide or manganese dioxide and sulphuric acid, give off chlorine, *e.g.:*

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

Chlorides distilled with sulphuric acid and potassium chromate, yield a dark bluish-red distillate of chromic oxychloride. Some metallic chlorides are decomposed by *water*, forming hydrochloric acid and an oxychloride, *e.g.:* $BiCl_3 + H_2O = 2HCl + BiClO$. The chlorides of antimony and stannous chloride are decomposed in a similar manner.

All soluble chlorides give with solution of *silver nitrate* a white

precipitate of silver chloride, easily soluble in ammonia, insoluble in nitric acid. With *mercurous nitrate*, they yield a white curdy precipitate of mercurous chloride, blackened by ammonia; and with *lead-salts*, not too dilute, a white precipitate of lead chloride, soluble in excess of water.

Metallic chlorides unite with each other and with the chlorides of the non-metallic elements, forming such compounds as potassium chloromercurate, $2KCl,HgCl_2$, sodium chloroplatinate, $2NaCl,PtCl_4$, potassium chloriodate, KCl,ICl_3, &c. Metallic chlorides combine in definite proportions with ammonia and organic bases: the chlorides of platinum form with ammonia the compounds $2NH_3,PtCl_2$, $4NH_3,PtCl_2$, $2NH_3,PtCl_4$, and $4NH_3,PtCl_4$; mercuric chloride forms with aniline the compound $2C_6H_7N,HgCl_2$, &c.

Chlorides also unite with oxides and sulphides, forming *oxychlorides* and *sulphochlorides*, which may be regarded as chlorides having part of their chlorine replaced by an equivalent quantity of oxygen or sulphur (Cl_2 by O or S). Bismuth, for example, forms an oxychloride having the composition BiClO or $BiCl_3,Bi_2O_3$.

Bromides.—Bromine unites directly with most metals, forming compounds analogous in composition to the chlorides, and resembling them in most of their properties. The bromides of the alkali-metals occur in sea-water and in many saline springs; silver bromide occurs as a natural mineral. Nearly all bromides are soluble in water, and may be formed by treating an oxide, hydroxide, or carbonate with hydrobromic acid, the solutions when evaporated giving off water for the most part, and leaving a solid metallic bromide; some of them, however, namely, the bromides of magnesium, aluminium, and the other earth-metals, are more or less decomposed by evaporation, giving off hydrobromic acid, and leaving a mixture of metallic bromide and oxide. Silver bromide and mercurous bromide are insoluble in water, and lead bromide is very sparingly soluble; these are obtained by precipitation.

Metallic bromides are solid at ordinary temperatures; most of them fuse at a moderate heat, and volatilise at higher temperatures. The bromides of gold and platinum are decomposed by mere exposure to heat; many others give up their bromine when heated in contact with the air. *Chlorine*, with the aid of heat, drives out the bromine and converts them into chlorides. *Hydrochloric acid* also decomposes them at a red heat, giving off hydrobromic acid. Strong *sulphuric* or *nitric acid* decomposes them, with evolution of hydrobromic acid, which, if the sulphuric or nitric acid is concentrated, and in excess, is partly decomposed, with separation of bromine and formation of sulphurous oxide or nitrogen dioxide. Bromides heated with *sulphuric acid* and *manganese dioxide* or *potassium chromate*, give off free bromine.

Bromides in solution are easily decomposed by chlorine, either in the form of gas or dissolved in water, the liquid acquiring a red or reddish-yellow colour, according to the quantity of bromine present;

and on agitating the liquid with ether, that liquid dissolves the bromine, forming a red solution, which rises to the surface.

Soluble bromides give with *silver nitrate* a white precipitate of silver bromide, greatly resembling the chloride, but much less soluble in ammonia, insoluble in hot nitric acid. *Mercurous nitrate* produces a yellowish-white precipitate; and *lead acetate* a white precipitate much less soluble in water than the chloride. *Palladium nitrate* produces in solutions of bromides not containing chlorine, a black precipitate of bromide. Palladium chloride produces no precipitate; neither does the nitrate, if soluble chlorides are present.

Bromides unite with each other in the same manner as chlorides; also with oxides, sulphides, and ammonia.

Iodides.—These compounds are obtained by processes similar to those which yield the chlorides and bromides. Many metals unite directly with iodine. Potassium and sodium iodides exist in sea-water and in many salt-springs; silver iodide occurs as a natural mineral.

Metallic iodides are analogous to the bromides and chlorides in composition and properties. But few of them are decomposed by heat alone; the iodides of gold, silver, platinum, and palladium, however, give up their iodine when heated.

Most metallic iodides are perfectly soluble in water; but lead iodide is very slightly soluble, and the iodides of mercury and silver are quite insoluble.

Solutions of iodides evaporated out of contact of air, generally leave anhydrous metallic iodides, which partly separate in the crystalline form before the water is wholly driven off. The iodides of the earth-metals, however, are resolved, on evaporation, into the earthy oxides and hydriodic acid, which escapes. A very small quantity of *chlorine* colours the solution yellow or brown, by partial decomposition; and a somewhat larger quantity takes up the whole of the metal, forming a chloride, and separates the iodine, which then gives a blue colour with starch; a still larger quantity of chlorine gives the liquid a paler colour, and converts the separated iodine into trichloride of iodine, which does not give a blue colour with starch, and frequently enters into combination with the metallic chloride produced. Strong *sulphuric acid* and somewhat concentrated *nitric acid* colour the solution yellow or brown; and if the quantity of the iodide is large, and the solution much concentrated or heated, they liberate iodine, which partly escapes in violet vapours. *Starch* mixed with the solution, even if it be very dilute, is turned blue—permanently when the decomposition is effected by sulphuric acid; for a time only when it is effected by nitric acid, especially if that acid be added in large quantity.

The aqueous solution of an iodide gives a brown precipitate with *salts of bismuth;* orange-yellow with *lead* salts; dirty-white with *cuprous salts*, also with *cupric* salts, especially on the addition of *sulphurous acid*; greenish-yellow with *mercurous* salts; scarlet with

mercuric salts; yellowish-white with *silver* salts; lemon-yellow with *gold* salts; brown with *platinic* salts—first, however, turning the liquid dark brown-red; and black with salts of *palladium*, even when extremely dilute. All these precipitates consist of metallic iodides, many of them soluble in excess of the soluble iodide: the silver precipitate is insoluble in nitric acid and very little soluble in ammonia.

Metallic iodides unite with one another, forming double iodides, analogous to the double chlorides; they also absorb ammonia gas in definite proportions. Some of them, as those of antimony and tellurium, unite with the oxides of the corresponding metals, forming oxyiodides.

Fluorides.—These compounds are formed—1. By heating hydrofluoric acid with certain metals. 2. By the action of that acid on metallic oxides. 3. By heating electro-negative metals—antimony, for example—with fluoride of lead or fluoride of mercury. 4. Volatile metallic fluorides may be prepared by heating fluor-spar with sulphuric acid and the oxide of the metal.

Fluorides have no metallic lustre; most of them are easily fusible, and for the most part resemble the chlorides. They are not decomposed by ignition, either alone or when mixed with charcoal. When ignited in contact with the air, in a flame which contains aqueous vapour, many of them are converted into oxides, while the fluorine is given off as hydrofluoric acid. All fluorides are decomposed by *chlorine*, and converted into chlorides. They are not decomposed by *phosphoric oxide* unless silica is present. They are decomposed at a gentle heat by strong *sulphuric acid*, with formation of metallic sulphate and evolution of hydrofluoric acid.

The fluorides of tin and silver are easily soluble in water; those of potassium, sodium, and iron are sparingly soluble; those of strontium and cadmium very slightly soluble, and the rest insoluble. The solutions of ammonium, potassium, and sodium fluoride have an alkaline reaction. The aqueous solutions of fluorides corrode glass vessels in which they are kept or evaporated. They form with soluble *calcium salts* a precipitate of calcium fluoride, in the form of a transparent jelly, which is scarcely visible, because its refractive power is nearly the same as that of the liquid; the addition of ammonia makes it plainer. This precipitate, if it does not contain silica, dissolves with difficulty in hydrochloric or nitric acid, and is re-precipitated by ammonia. The aqueous fluorides give a pulverulent precipitate with lead acetate.

The fluorides of antimony, arsenic, chromium, mercury, niobium, osmium, tantalum, tin, titanium, tungsten, and zinc, are volatile without decomposition.

Fluorine has a great tendency to form double salts, consisting of a fluoride of a basic or positive metal united with the fluoride of hydrogen, boron, silicon, tin, titanium, zirconium, &c., e.g.—

Potassium hydrofluoride	KHF_2	$= KF,HF$
Potassium borofluoride	KBF_4	$= KF,BF_3$
Potassium silicofluoride	K_2SiF_6	$= 2KF,SiF_4$
Potassium titanofluoride	K_2TiF_6	$= 2KF,TiF_4$
Potassium stannofluoride	K_2SnF_6	$= 2KF,SnF_4$
Potassium zircofluoride	K_2ZrF_6	$= 2KF,ZrF_4$

The four classes of compounds just described, the chlorides, bromides, iodides, and fluorides, form a group often designated as haloïd compounds or haloïd* salts, from their analogy to sodium chloride or sea-salt, which may be regarded as a type of them all. The elements, chlorine, bromine, iodine, and fluorine, are called halogens.

Cyanides.—Closely related to these haloïd compounds are the cyanides, formed by the union of metals with the group CN, cyanogen, CN (p. 265).

Some metals—potassium among the number—are converted into cyanides by heating them in cyanogen gas or vapour of hydrocyanic acid. The cyanides of the alkali-metals are also formed (together with cyanates) by passing cyanogen gas over the heated hydroxides or carbonates of the same metals; potassium cyanide also, by passing nitrogen gas over a mixture of charcoal and hydroxide or carbonate of potassium at a bright red heat. Cyanides are formed abundantly when nitrogenous organic compounds are heated with fixed alkalis. Other modes of formation will be mentioned hereafter.

The cyanides of the alkali-metals, and of barium, strontium, calcium, magnesium, and mercury, are soluble in water, and may be produced by treating the corresponding oxides or hydroxides with hydrocyanic acid. Nearly all other metallic cyanides are insoluble, and are obtained by precipitation from the soluble cyanides.

The cyanides of the alkali-metals sustain a red heat without decomposition, provided air and moisture be excluded. The cyanides of many of the heavy metals, as lead, iron, cobalt, nickel, and copper, under these circumstances, give off all their nitrogen as gas, and leave a metallic carbonate; mercuric cyanide is resolved into mercury and cyanogen gas; silver cyanide gives off half its cyanogen as gas. Most cyanides, when heated with dilute acids, give off their cyanogen as hydrocyanic acid.

Cyanides have a strong tendency to unite with one another, forming double cyanides. The most important of these are the double cyanides of iron and potassium, namely, *potassio-ferrous cyanide*, $Fe''K_4(CN)_6$, commonly called yellow prussiate of potash; and *potassio-ferric cyanide*, $Fe'''K_3(CN)_6$, commonly called red prussiate of potash. Both these are splendidly crystalline salts, which dis-

* From ἅλς, the sea.

solve easily in water, and form highly characteristic precipitates with many metallic salts. These salts, with the other cyanides, will be more fully described under "Organic Chemistry;" but they are mentioned here, on account of their frequent use in the qualitative analysis of metallic solutions.

Oxides.—All metals combine with oxygen, and most of them in several proportions. In almost all cases oxides are formed corresponding in composition with the chlorides, one atom of oxygen taking the place of two atoms of chlorine. Many metals also form oxides to which no chlorine analogues are known; thus lead, which forms only one chloride, $PbCl_2$, forms, in addition to the monoxide, PbO, a dioxide, PbO_2, besides oxides of intermediate composition; osmium also, the highest chloride of which is $OsCl_4$, forms, in addition to the dioxide, a trioxide and a tetroxide. This arises from the fact that any number of atoms of oxygen or other dyad element may enter into a compound without disturbing the balance of equivalency (p. 287).

Just as chlorides are derived by substitution from hydrochloric acid, HCl (p. 337), so likewise may oxides be derived from one or more molecules of water, H_2O; but as the molecule of water contains two hydrogen-atoms, the replacement of the hydrogen may, as already explained (p. 269), be either total or partial, the product in the first case being an anhydrous metallic oxide, and in the second a hydrated oxide or hydroxide, in which the oxygen is associated both with hydrogen and with metal; in this manner the following hydroxides and anhydrous oxides may be constituted:

Type.	Hydroxides.	Oxides.
H_2O . . .	KHO . .	K_2O
		BaO
H_4O_2 . . .	BaH_2O_2 . .	SnO_2
	$BiHO_2$	
H_6O_3 . . .	$AsHO_3$ . .	Sb_2O_3
	SnH_2O_3 . .	WO_3
H_8O_4 . . .	ZrH_4O_4	
$H_{10}O_5$ . . .	. . . .	Sb_2O_5.

It may be observed that the hydroxides of artiad metals contain the elements of a molecule of the corresponding anhydrous oxide, and of one or more molecules of water, and may therefore also be regarded as hydrates; thus—

Barium hydroxide or hydrate .	$BaH_2O_2 = BaO,H_2O$
Stannic „ „ .	$SnH_2O_3 = SnO_2,H_2O$
Zirconium „ „ .	$ZrH_4O_4 = ZrO_2,2H_2O$.

But the hydroxide of a perissad metal contains in its molecule only

half the number of atoms required to make up a molecule of oxide together with a molecule of water; thus—

Potassium hydroxide . . . $KHO = \frac{1}{2}(K_2O,H_2O)$
Bismuth „ . . . $BiHO_2 = \frac{1}{2}(Bi'''_2O_3,H_2O)$.

These perissad hydroxides cannot, therefore, be correctly regarded as hydrates, that is, as compounds of anhydrous oxide and water.

Many metallic oxides occur as natural minerals, and some, especially those of iron, tin, and copper, in large quantities, forming ores from which the metals are extracted.

All metals, except gold, platinum, iridium, rhodium, and ruthenium, are capable of uniting directly with oxygen. Some, as potassium, sodium, and barium, oxidise rapidly on exposure to the air at ordinary temperatures, and decompose water with energy. Most metals, however, when in the massive state, remain perfectly bright and unacted on in dry air or oxygen gas, but oxidise slowly when moisture is present; such is the case with iron, zinc, and lead. Some of the ordinarily permanent metals, when in a very finely divided state, as lead when obtained by ignition of its tartrate, and iron reduced from its oxide by ignition in hydrogen gas, take fire and oxidise spontaneously as soon as they come in contact with the air. Lead, iron, copper, and the volatile metals, antimony, zinc, cadmium, and mercury, are converted into oxide when heated in air or oxygen. Many metals, especially at a red heat, are readily oxidised by water or steam. A very general method of preparing metallic oxides is to subject the corresponding hydroxides, carbonates, nitrates, sulphates, or any oxygen-salts containing volatile acids, to the action of heat.

Oxides are for the most part opaque earthy bodies, destitute of metallic lustre. The majority of them are fusible; those of lead and bismuth at a low red heat; those of copper and iron at a white heat; those of barium and aluminium before the oxy-hydrogen blow-pipe; while calcium oxide or lime does not fuse at any temperature to which it has yet been subjected. Oxides are, for the most part, much less fusible than the uncombined metals. Osmium tetroxide and antimony trioxide are readily volatile.

A greater or lesser degree of heat effects the decomposition of many metallic oxides. Those of gold, platinum, silver, and mercury are reduced to the metallic or reguline state by an incipient red heat. At a somewhat higher temperature, the higher oxides of barium, cobalt, nickel, and lead are reduced to the state of monoxides; while the trimetallic tetroxides of manganese and iron, Mn_3O_4 and Fe_3O_4, are produced by exposing manganese dioxide, MnO_2, and iron sesquioxide, Fe_2O_3, respectively to a still stronger heat. By gentle ignition, arsenic pentoxide is reduced to the state of trioxide, and chromium trioxide to sesquioxide.

The superior oxides of the metals are easily reduced to a lower state of oxidation by the action of a current of *hydrogen gas* at a

more or less elevated temperature. At a higher degree of heat, hydrogen gas will transform to the reguline state all metallic oxides except the sesquioxides of aluminium and chromium, and the monoxides of manganese, magnesium, barium, strontium, calcium, lithium, sodium, and potassium. The temperature necessary to enable hydrogen to effect the decomposition of some oxides is comparatively low. Thus metallic iron may be reduced from its oxides by hydrogen gas at a heat considerably below redness. *Carbon*, at a red or white heat, is a still more powerful deoxidising agent than hydrogen, and seems to be capable of completely reducing all metallic oxides whatsoever. The oxidisable metals in general act as reducing agents.

Chlorine decomposes all metallic oxides, except those of the earth-metals, converting them into chlorides, and expelling the oxygen. With silver oxide this reaction takes place at ordinary temperatures; with the alkalis and alkaline earths, at a full red heat. *Sulphur*, at high temperatures, can decompose most metallic oxides; with many oxides—those of silver, mercury, lead, and copper, for instance—metallic sulphides and sulphur dioxide are produced; with the highly basylous oxides, the products are metallic sulphate and sulphide. There are some oxides upon which sulphur exerts no action. Of these the principal are magnesia, alumina, chromic, stannic, and titanic oxides. By boiling sulphur with soluble hydroxides, mixtures of polysulphide and thiosulphate are produced. With the exception of magnesia, alumina, and chromic oxide, most metallic oxides can absorb sulphuretted hydrogen, to form metallic sulphide or hydrosulphide and water.

Oxygen-salts or **Oxysalts.**—It has been already explained in the Introduction that oxides may be divided into three classes, *acid*, *neutral*, and *basic*, the first and third being capable of uniting with one another in definite proportions, and forming compounds called salts. The most characteristic of the acid oxides are those of certain metalloids, as nitrogen, sulphur, and phosphorus, which unite readily with water or the elements of water, forming compounds called oxygen-acids, distinguished by sour taste, solubility in water, and the power of reddening certain vegetable blue colours. The most characteristic of the basic oxides, on the other hand, are those of the alkali-metals and alkaline earth-metals (p. 335), which likewise dissolve in water, but form alkaline solutions, possessing in an eminent degree the power of *neutralising* acids and forming salts with them. The same power is exhibited more or less by the monoxides of most other metals, as zinc, iron, copper, manganese, &c., and by the sesquioxides of aluminium, iron, chromium, and others. The higher oxides of several of these metals—the trioxides of chromium, for example—exhibit acid characters, being capable of forming salts with the more basic oxides; and some metals, as antimony, niobium, and tantalum, form only acid oxides.

In some cases salts are formed by the direct combination of an

acid and a basic oxide. Thus, when vapour of sulphuric oxide, SO_3, is passed over red-hot barium oxide, BaO, the two combine together, and form barium sulphate, BaO,SO_3 or $BaSO_4$. Silicic oxide, SiO_2, phosphoric oxide, P_2O_5, boric oxide, B_2O_3, and other acid oxides capable of withstanding a high temperature without decomposing or volatilising, likewise unite with basic oxides when heated with them, and form salts.

But in the majority of cases metallic salts are formed by substitution, or interchange of a metal for hydrogen, or of one metal for another. It is clear, indeed, that any metallic salt (zinc sulphate, ZnO,SO_3, for example) may be derived from the corresponding acid or hydrogen salt (H_2O,SO_3) by substitution of a metal for an equivalent quantity of hydrogen. Accordingly, metallic salts are frequently produced by the action of an acid on a metal or a metallic oxide or hydroxide, thus—

(1.) $H_2SO_4 + Zn = ZnSO_4 + H_2$.
(2.) $2HNO_3 + Ag_2O = 2AgNO_3 + H_2O$.
(3.) $HNO_3 + KHO = KNO_3 + H_2O$.

In the instances represented by these equations, the metallic salts formed are soluble in water. Insoluble salts are frequently prepared by interchange of the metals between two soluble salts, barium nitrate and sodium sulphate, for example, thus—

(4.) $Ba(NO_3)_2 + Na_2SO_4 = BaSO_4 + 2NaNO_3$.

In this case the barium sulphate, being insoluble, is precipitated, while the sodium nitrate remains in solution.

In all these reactions, hydrochloric acid or a metallic chloride might be substituted for the oxygen-acid or oxygen-salt, without the slightest alteration in the mode of action, the product formed in each case being a chloride instead of a nitrate or sulphate; thus:—

(1)′ $2HCl + Zn = ZnCl_2 + H_2$
(2)′ $2HCl + Ag_2O = 2AgCl + H_2O$
(3)′ $HCl + KHO = KCl + H_2O$
(4)′ $AgNO_3 + NaCl = AgCl + NaNO_3$.

From all these considerations it appears that oxygen-salts may be regarded, either as compounds of acid oxides with basic oxides, or as analogous in composition to chlorides,—that is to say, as compounds of a metal with a radicle or group of elements, such as NO_3 (*nitrione*) in the nitrates, SO_4 (*sulphione*), in the sulphates, discharging functions similar to those of chlorine, and capable, like that element, of passing unchanged from one compound to another.

For many years, indeed, it was a subject of discussion among chemists, whether the former or the latter of these views should be *regarded* as representing the *actual* constitution of oxygen salts.

Berzelius divided salts into two classes: 1. Haloïd salts, comprising, as already mentioned, the chlorides, bromides, iodides, and fluorides, which are compounds of a metal with a monad metallic element.—2. Amphid salts, consisting of an acid or electro-negative oxide, sulphide, selenide, or telluride, with a basic or electro-positive compound of the same kind; such as potassium arsenate, $3K_2O,As_2O_5$; potassium sulpharsenate, $3K_2S,As_2S_5$; potassium seleniophosphate, $2K_2Se,P_2Se_5$, &c.

Davy, on the other hand, observing the close analogy between the reactions of chlorides, on the one hand, and of oxygen-salts, such as sulphates, nitrates, &c., on the other, suggested that the latter might be regarded, like the former, as compounds of metals with acid or electro-negative radicles, the only difference being, that in the former the acid radicle is an elementary body, Cl,Br, &c., whereas in the former it is a compound, as SO_4, NO_5, PO_4, &c. This was called the *binary theory of salts;* it was supported by many ingenious arguments by its proposer and several contemporary chemists; in later years also by Liebig, and by Daniell and Miller, who observed that the mode of decomposition of salts by the electric current is more easily represented by this theory than by the older one (p. 316).

At the present day, the relative merits of these two theories are not regarded as a point of very great importance. Chemists, in fact, no longer attempt to construct formulæ which shall represent the actual arrangement of atoms in a compound, the formulæ now in use being rather intended to exhibit, first, the balance of neutralisation of the units of equivalency or combining capacity of the several elements contained in a compound (p. 282); and, secondly, the manner in which any compound or group of atoms splits up into subordinate groups under the influence of different reagents. According to the latter view, a compound containing three or more elementary atoms may be represented by different formulæ corresponding with the several ways in which it decomposes. Thus hydrogen sulphate or sulphuric acid, H_2SO_4, may be represented by either of the following formulæ:—

1. H_2SO_4, which represents the separation of hydrogen and formation of a metallic sulphate, by the action of zinc, &c.; this is the formula corresponding with the binary theory of salts.

2. SO_3,H_2O. This formula represents the formation of the acid by direct hydration of sulphuric oxide; the separation of water and formation of a metallic sulphate by the action of magnesia and other anhydrous oxides; and the separation of sulphuric oxide and formation of phosphoric acid by the action of phosphoric oxide:—

$$SO_3,H_2O + MgO = SO_3,MgO + H_2O$$
$$SO_3,H_2O + P_2O_5 = P_2O_5,H_2O + SO_3.$$

3. SO_2,O_2H_2, or $SO_2(OH)_2$. This formula represents such reactions as the elimination of hydrogen dioxide by the action of barium dioxide, BaO_2.

CÆSIUM AND RUBIDIUM.

Cs = 133. Rb = 85·4.

THE two metals designated by these names were discovered by Bunsen and Kirchhoff by means of their spectrum apparatus mentioned on page 89 : the former in 1860 and the latter in 1861. These metals, it appears, are widely diffused in nature, but always occur in very small quantities: they have been detected in many mineral waters, as well as in some minerals, namely, lithia-mica or lepidolite, and petalite; lately also in felspar; they have also been found in the alkaline ashes of beetroot. The salt-spring of Dürkheim, which contains 0·17 part of cæsium chloride in a million parts of water, was till lately regarded as the richest source of cæsium; but from experiments by Colonel Yorke,* it appears that the hot spring of Wheal Clifford, already mentioned as a source of lithium, contains 1·71 parts of cæsium chloride in a million, or 0·12 grain in a gallon. According to Cossa,† a very rich source of these metals is found in the alum of "la Schicciola," in Vulcano, one of the Lipari Islands.

The best material for the preparation of rubidium is lepidolite, which has been found to contain as much as 0·2 per cent. of that metal. Both metals are closely allied to potassium in their deportment.

Rubidium and cæsium, like potassium, form double salts with tetrachloride of platinum, which are, however, much less soluble than the corresponding potassium salts: it is on this property that the separation of these metals from potassium is based. The mixture of platinochlorides is repeatedly extracted with boiling water, when a difficultly soluble residue, consisting chiefly of the platinochlorides of cæsium and rubidium, remains; and these two metals are finally separated by converting them into tartrates, rubidium tartrate requiring for solution eight times as much water as cæsium tartrate, and therefore crystallising out first from the mixed solution. According to Cossa (*loc. cit.*), the separation is best effected by treating a solution of cæsium and rubidium alums with antimony trichloride, which throws down the whole of the cæsium, leaving the rubidium in solution.

The hydroxides of these metals are powerful bases, which attract carbonic acid from the air, passing first into normal and then into acid carbonates. Cæsium carbonate is soluble in absolute alcohol; rubidium carbonate is nearly insoluble in that liquid: this property is made use of for the separation of these two metals. Cæsium chloride crystallises in cubes, and is somewhat more soluble in water than chloride of potassium.

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* Journal of the Chemical Society, 1872, p. 273.

† Gazzetta chimica italiana, 1878, p. 225; Chem. Soc. J., xxxiv. 953. See also Setterberg, *ibid.*, xliv. 464.

Rubidium chloride, in the fused state, is easily decomposed by the electric current; the metal produced rises to the surface and burns with a reddish light. If this experiment be performed in an atmosphere of hydrogen, to prevent oxidation, the separated metal is nevertheless lost, dissolving in the fused chloride, which is transformed into a subchloride having the blue colour of smalt.

Rubidium, when separated under mercury by the electric current, forms a silvery crystalline amalgam, which oxidises rapidly on exposure to the air, and decomposes water at ordinary temperatures.

Metallic cæsium cannot readily be obtained, either by the electrolysis of its chloride, or by heating its acid tartrate with sugar, charcoal, and chalk, but it may be prepared by electrolysis of its cyanide, which is formed on passing anhydrous hydrocyanic acid into a solution of cæsium hydroxide in absolute alcohol. To prepare the metal, a mixture of barium cyanide (1 pt.) and cæsium cyanide (4 pts.) is fused in a porcelain crucible, and an electric current is passed through the molten mass, aluminium poles being used. On warming the contents of the crucible under petroleum, the metal separates in globules. Metallic cæsium is silver-white, like potassium and rubidium, and soft at ordinary temperatures; sp. gr. 1·88 at 15°; melting point 26—27°. It oxidises quickly in the air, and takes fire when thrown on water (Setterberg).

AMMONIUM.

The ammonia salts are most conveniently studied in this place, on account of their close analogy to those of potassium and sodium. These salts are formed by the direct union of ammonia, NH_3, with acids, and as already pointed out (p. 209), they may be regarded as compounds of acid radicles, Cl, NO_3, SO_4, &c., with a basylous radicle, NH_4, called ammonium, which plays in these salts the same part as potassium and sodium in their respective compounds; thus:—

NH_3	+	HCl	=	$NH_4.Cl$
Ammonia.		Hydrochloric acid.		Ammonium chloride.
NH_3	+	HNO_3	=	$NH_4.NO_3$
		Nitric acid.		Ammonium nitrate.
NH_3	+	H_2SO_4	=	$NH_4.SO_4H.$
		Sulphuric acid.		Acid ammonium sulphate.
$2NH_3$	+	H_2SO_4	=	$(NH_4)_2SO_4.$
				Normal ammonium sulphate.

The radicle NH_4 is not capable of existing in the free state, inasmuch as it contains an uneven number of monad atoms: it is simply the residue which is left on removing the atom of chlorine from the saturated molecule, NH_4Cl. Whether the double molecule N_2H_8, or $\begin{matrix}NH_4\\|\\NH_4\end{matrix}$, has a separate existence, is a different question. Ammonium is said, indeed, to be capable of forming an amalgam with mercury; but even in this state it is quickly resolved into ammonia and free hydrogen.

When a globule of mercury is placed on a piece of moistened potassium hydroxide, and connected with the negative side of a voltaic battery of very moderate power, the circuit being completed through the platinum plate upon which the alkali rests, decomposition of the latter takes place, and an amalgam of potassium is rapidly formed. If this experiment be now repeated with a piece of sal-ammoniac instead of potassium hydroxide, a soft, solid, metalline mass is also produced, which has been called the *ammoniacal amalgam*, and considered to contain ammonium in combination with mercury. A simpler method of preparing this compound is the following:—A little mercury is put into a test-tube with a grain or two of potassium or sodium, and gentle heat is applied; combination ensues, attended by heat and light. When cold, the fluid amalgam is put into a capsule, and covered with a strong solution of sal-ammoniac. The production of an ammoniacal amalgam instantly commences, the mercury increasing prodigiously in volume, and becoming quite pasty. The increase of weight is, however, quite trifling, varying from $\frac{1}{1800}$ to $\frac{1}{1200}$ part. Left to itself, the amalgam quickly decomposes into fluid mercury, ammonia, and hydrogen. It is most probable, indeed, that the so-called amalgam may be nothing more than mercury which has absorbed a certain quantity of these gases; just as silver, when heated to a very high temperature, is capable of taking up about twenty times its volume of oxygen gas, which it gives up again on cooling.*

But whether ammonium has any separate existence or not, it is quite certain that many ammoniacal salts are isomorphous with those of potassium; and if from any two of the corresponding salts, as the nitrates KNO_3 and NH_4NO_3, we subtract the radicle NO_3 common to the two, there remain the metal K and the group NH_4, which are, therefore, supposed to be isomorphous.

Ammonium Chloride, Sal-ammoniac, NH_4Cl or NH_3,HCl.—Sal-ammoniac was formerly obtained from Egypt, being extracted by sublimation from the soot of camels' dung: it is now largely

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* See Watts's Dictionary of Chemistry, vol. vi. p. 718.

manufactured from the ammoniacal liquid of the gas works, and from the condensed products of the distillation of bones and other animal refuse, in the preparation of animal charcoal.

These impure and highly offensive solutions are treated with a slight excess of hydrochloric acid, by which the free alkali is neutralised, and the carbonate and sulphide are decomposed, with evolution of carbonic acid and sulphuretted hydrogen gases. The liquid is evaporated to dryness, and the salt carefully heated, to expel or decompose the tarry matter; it is then purified by sublimation in large iron vessels lined with clay, surmounted with domes of lead. Sublimed sal-ammoniac has a fibrous texture; and is tough and difficult to powder.

Sal-ammoniac separates from its aqueous solution in radiate groups of small but distinct cubes and octohedrons. It has a sharp saline taste, and dissolves in $2\frac{3}{4}$ parts of cold, and in a much smaller quantity of hot water. By heat, it is sublimed without decomposition. The crystals are anhydrous. Ammonium chloride forms double salts with the chlorides of magnesium, nickel, cobalt, manganese, zinc, and copper.

Ammonium Sulphate, $(NH_4)_2SO_4$.—Prepared by neutralising ammonium carbonate with sulphuric acid, or on the large scale, for use as a manure, by adding sulphuric acid in excess to the coal-gas liquor just mentioned, and purifying the product by suitable means. It is soluble in 2 parts of cold water, and crystallises in long, flattened, six-sided prisms. It is entirely decomposed and driven off by ignition, and, even to a certain extent, by long boiling with water, ammonia being expelled and the liquid rendered acid.

Ammonium Nitrate, $(NH_4)NO_3$, is easily prepared by adding ammonium carbonate to slightly diluted nitric acid until neutralisation has been reached. By slow evaporation at a moderate temperature it crystallises in six-sided prisms, like those of potassium nitrate; but, as usually prepared for making nitrogen monoxide, by quick boiling until a portion solidifies completely on cooling, it forms a fibrous and indistinct crystalline mass.

Ammonium nitrate dissolves in 2 parts of cold water, producing considerable depression of temperature; it is but feebly deliquescent, and deflagrates like nitre on contact with heated combustible matter. Its decomposition by heat has been already explained (p. 216).

Ammonium Phosphates.—The *Normal* or *Triammonic salt*, $(NH_4)_3PO_4$, is obtained as a crystalline mass when the di-ammonic salt is supersaturated with strong aqueous ammonia, and crystallises from dilute ammonia in short prismatic needles containing 3 molecules of water. The salt decomposes when its aqueous solution is boiled, giving off two-thirds of its ammonia.—The *di-ammonic salt*,

$(NH_4)_2HPO_4$, occurs in guano from Ichaboe, and is deposited in transparent monoclinic prisms, when an aqueous solution of phosphoric acid containing excess of ammonia is left to evaporate.—The *mono-ammonic salt*, $(NH_4)_2HPO_4$, formed when aqueous phosphoric acid is added to aqueous ammonia till the solution becomes acid and is no longer precipitated by barium chloride, crystallises in quadratic prisms, isomorphous with the corresponding potassium salt.

Sodium, Ammonium, and Hydrogen Phosphate; Phosphorus Salt; Microcosmic Salt, $Na(NH_4)HPO_4,4H_2O$.—Six parts of common sodium phosphate are heated with 2 parts of water, until the whole is liquefied, and 1 part of powdered sal-ammoniac is added; common salt then separates, and may be removed by a filter; and from the solution, duly concentrated, the microcosmic salt is deposited in prismatic crystals, which may be purified by one or two re-crystallisations. Microcosmic salt is very soluble. When gently heated, it parts with its 4 molecules of crystallisation-water, and, at a higher temperature, the basic hydrogen is likewise expelled as water, together with ammonia, and a very fusible compound, sodium metaphosphate, remains, which is valuable as a flux in blow-pipe experiments. Microcosmic salt occurs in decomposed urine.

Ammonium Carbonates.—There are three definite carbonates of ammonia, the composition of which is as follows:—

Normal or Diammonic carbonate,	$(NH_4)_2CO_3,H_2O$
Acid or Ammonio-hydric carbonate,	$(NH_4)HCO_3$
Half-acid, or Tetrammonio-dihydric carbonate,	$(NH_4)_4H_2(CO_3)_3,H_2O$.

(1.) The *normal carbonate* is prepared by addition of ammonia to one of the acid salts, or of water to the carbamate of ammonia, CON_2H_6 (p. 396), with certain special precautions, the description of which is too long for insertion in this work, to prevent the escape of a portion of the ammonia. It crystallises in elongated plates or flattened prisms, having a caustic taste, a powerful ammoniacal odour, and easily giving off ammonia and water, whereby they are converted into the acid carbonate:

$$(NH_4)_2CO_3,H_2O = NH_3 + H_2O + (NH_4)HCO_3.$$

(2.) *Ammonium and Hydrogen Carbonate*, or *Mono-ammonic Carbonate*, $(NH_4)HCO_3$, commonly called *Bicarbonate*, or *Acid carbonate of ammonia*.—This salt is obtained by saturating an aqueous solution of ammonia, or of the half-acid carbonate, with carbonic acid gas; or by treating the finely pounded half-acid carbonate with strong alcohol, which dissolves out normal or di-ammonic carbonate, leaving a residue of the mono-ammonic salt. Cold water may be used instead of alcohol for this purpose; but it

dissolves a larger quantity of the mono-ammonic carbonate. All ammonium carbonates when left to themselves are gradually converted into mono-ammonic carbonate. This salt forms large crystals belonging to the trimetric system. According to Deville it is dimorphous, but never isomorphous with monopotassic carbonate; when exposed to the air, it volatilises slowly, and gives off a faint ammoniacal odour. It dissolves in 8 parts of cold water, the solution decomposing gradually at ordinary temperatures, quickly when heated above 30°, with evolution of ammonia. It is insoluble in alcohol, but when exposed to the air, under alcohol, it dissolves as normal carbonate, evolving carbon dioxide.

It has been found native in considerable quantity in the deposits of guano on the western coast of Patagonia, in white crystalline masses, having a strong ammoniacal odour.

(3.) *Tetrammonio-dihydric Carbonate*, $N_4H_{18}C_3O_9 = (NH_4)_4H_2(CO_3)_3$. —This salt, also called *Half-acid Carbonate* or *Sesqui-carbonate of ammonia*, contains the elements of 1 molecule of di-ammonic and 2 molecules of mono-ammonic carbonate, into which it is, in fact, resolved by treatment with water or alcohol:

$$(NH_4)_4H_2(CO_3)_3 = (NH_4)_2CO_3 + 2(NH_4)HCO_3.$$

It is obtained by dissolving the commercial carbonate in strong aqueous ammonia, at about 30°, and crystallising the solution. It forms large transparent rectangular prisms, having their summits truncated by octohedral faces. These crystals decompose very rapidly in the air, giving off water and ammonia, and being converted into mono-ammonic carbonate.

Commercial carbonate of ammonia (*sal volatile, salt of hartshorn*) consists of half-acid carbonate more or less mixed with carbamate. It is prepared on the large scale by the dry distillation of bones, hartshorn, and other animal matter, and is purified from adhering empyreumatic oil by subliming it once or twice with animal charcoal in cast-iron vessels, over which glass receivers are inverted. Another method consists in heating to redness a mixture of 1 part ammonium chloride or sulphate, and 2 parts calcium carbonate (chalk), or potassium carbonate, in a retort to which a receiver is luted.

An elaborate description of the carbonates of ammonia has been published by Dr. Divers*, to whom is due the discovery of the normal ammonium carbonate.

Ammonium Sulphides.—Several of these compounds exist, and may be formed by distilling with sal-ammoniac the corresponding sulphides of potassium or sodium.

Ammonium and Hydrogen Sulphide, or *Ammonium Hydrosulphide*, $(NH_4)HS$, is a compound of great practical utility; it is

* Journal of the Chemical Society, 1870, pp. 171–279.

obtained by saturating a solution of ammonia with well-washed sulphuretted hydrogen gas, until no more of the latter is absorbed. The solution is nearly colourless at first, but becomes yellow after a time, without, however, suffering material injury, unless it has been exposed to the air. It gives precipitates with most metallic solutions, which are very often characteristic, and is of great service in analytical chemistry.

Ammoniacal salts are easily recognised ; they are all decomposed or volatilised at a high temperature ; and when heated with calcium hydroxide or solution of alkaline carbonate, they give off ammonia, which may be recognised by its odour and alkaline reaction. The salts are all more or less soluble, the acid tartrate and the platinochloride being, however, among the least soluble : hence ammonium salts cannot be distinguished from potassium salts by the tests of tartaric acid and platinum solution. When a solution containing an ammoniacal salt, or free ammonia, is mixed with potash, and a solution of *mercuric iodide* in *potassium iodide* is added, a brown precipitate or coloration is immediately produced, consisting of dimercurammonium iodide, NHg_2I :

$$NH_3 + 2HgI_2 = NHg_2I + 3HI.$$

This is called Nessler's test ; it is by far the most delicate test for ammonia that is known.

Amic Acids and Amides.

Sulphamic Acid.—When dry ammonia gas is passed over a thin layer of sulphuric oxide, SO_3, the gas is absorbed, and a white crystalline powder is formed, having the composition $N_2H_6SO_3$, that is, of ammonium sulphate minus one molecule of water :—

$$N_2H_6SO_3 = (NH_4)_2SO_4 - H_2O.$$

It is not, however, a salt of sulphuric acid : for its aqueous solution does not give any precipitate with baryta-water or soluble barium salts. It is, in fact, the ammonium salt of sulphamic acid, an acid derived from sulphuric acid, SO_4H_2 or $SO_2(HO)_2$, by substitution of the univalent radicle, NH_2 (p. 288), for one atom of hydroxyl, HO. The formula of this acid is $SO_2(NH_2)(OH)$, and that of its ammonium salt, $SO_2(NH_2)(ONH_4)$, or $SO_3N_2H_6$. Ammonium sulphamate is permanent in the air, and dissolves without decomposition in water. Its solution evaporated in a vacuum over oil of vitriol, yields the salt in transparent colourless crystals.

The solution of the ammonium salt, mixed with baryta-water, gives off ammonia, and yields a solution of *barium sulphamate*, $[SO_2(NH_2)O]_2Ba$, which may be obtained by evaporation in well-

defined crystals; and the solution of this salt, decomposed with potassium sulphate, yields *potassium sulphamate*, $SO_2(NH_2)(OK)$.

Carbamic Acid.—When dry ammonia gas is mixed with carbon dioxide, the mixture being kept cool, the gases combine in the proportion of 2 volumes of the former to 1 volume of the latter, forming a pungent, very volatile substance, which condenses in white flocks. This substance has the composition $CO_2N_2H_6$, that is, of normal ammonium carbonate, $CO_3(NH_4)_2$, *minus* one molecule of water. It exists, as already observed, in commercial carbonate of ammonia (p. 395). It was formerly called *anhydrous carbonate of ammonia;* but, like the preceding salt, it is not really a carbonate, but the ammonium salt of carbamic acid, $CO(NH_2)OH$, an acid derived from carbonic acid, CO_3H_2 or $CO(OH)_2$, by substitution of amidogen, NH_2, for one hydroxyl-group. Ammonium carbamate dissolves readily in water, and quickly takes up one molecule of that compound, whereby it is converted into normal ammonium carbonate. When treated with sulphuric oxide, it is converted into ammonium sulphamate.

Carbamide, CON_2H_4, or $CO(NH_2)_2$.—When ammonia gas is mixed with carbon oxychloride or phosgene gas, $COCl_2$, a white crystalline powder is formed, having this composition:—

$$COCl_2 + 2NH_3 = 2HCl + CON_2H_4.$$

This compound, which is likewise formed in other reactions to be afterwards considered, is derived from carbonic acid, $CO(OH)_2$, by substitution of 2 atoms of amidogen for 2 atoms of hydroxyl. It differs from carbamic acid in being a neutral substance, not containing any hydrogen easily replaceable by metals.

Other bibasic acids likewise yield an amic acid and a neutral amide by substitution of 1 or 2 atoms of amidogen for hydroxyl. Tribasic acids yield in like manner two amic acids and one neutral amide, and quadribasic acids may yield three amic acids and a neutral amide; thus, from pyrophosphoric acid, $P_2O_7H_4 = P_2O_3(OH)_4$, are obtained the three amic acids $P_2O_3(NH_2)(OH)_3$, $P_2O_3(NH_2)_2(OH)_2$ and $P_2O_3(NH_2)_3OH$.

Monobasic acids, which contain but one atom of hydroxyl, yield by this mode of substitution only neutral amides, no amic acids: thus, from acetic acid, $C_2H_4O_2 = C_2H_3O(OH)$, is obtained acetamide, $C_2H_3O(NH_2)$.

By similar substitution of metals, or of basylous compound radicles, for the hydrogen of ammonia, basic compounds, called amines, are formed. Thus, when potassium is gently heated in ammonia gas, *monopotassamine*, NH_2K, is formed. It is an olive-green substance, which is decomposed by water into ammonia and potassium hydroxide:—

$$NH_2K + H_2O = NH_3 + KHO.$$

It melts at a little below 100°, and when heated in a close vessel, is resolved into ammonia and *tripotassamine:*—

$$3NH_2K = 2NH_3 + NK_3.$$

The latter effervesces violently with water, yielding ammonia and potassium hydroxide:—

$$NK_3 + 3H_2O = NH_3 + 3KHO.$$

The formation and properties of amides and amines will be further considered under Organic Chemistry.

Metallammoniums.—These are hypothetical radicles derived from ammonium, N_2H_8, by substitution of metals for hydrogen. Salts of such radicles are formed in several ways. Ammonia gas is absorbed by various metallic salts in different proportions, forming compounds, some of which may be formulated as salts of metallammoniums. Thus, platinous chloride, $PtCl_2$, absorbs two molecules of ammonia, forming *platosammonium chloride*, $N_2H_6Pt''Cl_2$, and platinum tetrachloride, $PtCl_4$, absorbs four molecules of ammonia, forming *platinammonium chloride*, $N_4H_{12}Pt^{iv}Cl_4$. In like manner, cupric chloride and sulphate form the *chloride* and *sulphate of cuprammonium*, $N_2H_6Cu''Cl_2$ and $N_2H_6Cu''SO_4$.

Similar compounds are formed in many cases by precipitating metallic salts with ammonia or ammoniacal salts: thus, ammonia added to a solution of mercuric chloride, $HgCl_2$, forms a white precipitate, consisting of *dimercurammonium chloride*, $N_2H_4Hg''_2Cl_2$; and by dropping solution of mercuric chloride into a boiling solution of sal-ammoniac mixed with free ammonia, crystals are obtained, consisting of *mercurammonium chloride*, $N_2H_6Hg''Cl_2$. Some of these compounds will be further considered in connection with the several metals.

METALS OF THE ALKALINE EARTHS.

THE three metals, calcium, strontium, and barium, constituting this group, form oxides less soluble in water than the true alkalis, but exhibiting similar taste, causticity, and action on vegetable colours. These metals form but one chloride, *e.g.*, $CaCl_2$; their carbonates are insoluble in water; and barium sulphate is also insoluble, the sulphates of calcium and strontium slightly soluble.

CALCIUM.

Symbol, Ca. Atomic weight, 39·9.

CALCIUM is one of the most abundant and widely diffused of the metals, though it is never found in the free state. As carbonate, it occurs in a great variety of forms, constituting, as limestone, entire mountain ranges.

Calcium was obtained in an impure state by Davy, by means similar to those adopted for the preparation of barium (p. 409). Matthiessen prepared the pure metal by fusing a mixture of two molecules of calcium chloride and one of strontium chloride with some chloride of ammonium in a small porcelain crucible, in which an iron cylinder is placed as positive pole, and a pointed iron wire or a little rod of carbon connected with the zinc of the battery is made to touch the surface of the liquid. The reduced metal fuses and drops off from the point of the iron wire, and the bead is removed from the liquid by a small iron spatula. Liès-Bodart and Gobin prepare calcium by igniting the iodide with an equivalent quantity of sodium in an iron crucible having its lid screwed down.

Calcium is a light yellow metal of sp. gr. 1·5778. It is about as hard as gold, very ductile, and may be cut, filed, or hammered out into plates as thin as the finest paper. It tarnishes slowly in dry, more quickly in damp air, decomposes water quickly, and is still more rapidly acted upon by dilute acids. Heated on platinum foil over a spirit-lamp, it burns with a bright flash; with a brilliant light also when heated in oxygen or chlorine gas, or in vapour of bromine, iodine, or sulphur.

Calcium Chloride, $CaCl_2$, is usually prepared by dissolving marble in hydrochloric acid; it is also a bye-product in several chemical manufactures. It separates from a strong solution in colourless, prismatic, and exceedingly deliquescent crystals, which

contain six molecules of water. By heat this water is expelled, and by a temperature of strong ignition the salt is fused. The crystals reduced to powder are employed in the production of artificial cold by being mixed with snow or powdered ice; and the chloride, strongly dried, or in the fused state, is of great use in desiccating gases, for which purpose the latter are slowly transmitted through tubes filled with fragments of the salt. Calcium chloride is also freely soluble in alcohol, which, when anhydrous, forms with it a definite crystallisable compound.

The *bromide*, $CaBr_2$, and *iodide*, CaI_2, closely resemble the chloride.

Calcium Fluoride, Fluor-Spar, CaF_2, is important as the most abundant natural source of hydrofluoric acid and the other fluorides. It occurs beautifully crystallised, of various colours, in lead-veins, the crystals having commonly the cubic, but sometimes the octohedral form, parallel to the faces of which latter figure they always cleave. Some varieties, when heated, emit a greenish, and some a purple phosphorescent light. The fluoride is quite insoluble in water, and is decomposed by oil of vitriol in the manner already mentioned (p. 150).

Calcium Oxides.—The *Monoxide* or *Lime*, CaO, may be obtained in a state of considerable purity by heating to full redness for some time fragments of the black bituminous marble of Derbyshire or Kilkenny. If required absolutely pure, it must be made by igniting to whiteness, in a platinum crucible, an artificial calcium carbonate, prepared by precipitating the nitrate with ammonia carbonate. Lime in an impure state is prepared for building and agricultural purposes by calcining, in a kiln, the ordinary limestones which abound in many districts; a red heat, continued for some hours, is sufficient to disengage the whole of the carbonic acid. In the best contrived lime-kilns the process is carried on continuously, broken limestone and fuel being constantly thrown in at the top, and the burned lime raked out at intervals from beneath. Sometimes, when the limestone contains silica, and the heat has been very high, the lime refuses to slake, and is said to be *overburned;* in this case a portion of silicate has been formed.

Pure lime is white, and often very hard: it is quite infusible, and phosphoresces, or emits a pale light at a high temperature. When moistened with water, it slakes with great violence, evolving heat, and crumbling to a soft, white, bulky powder, which is a hydrate containing a single molecule of water, which can be again expelled by a red heat. This hydrate or hydroxide, CaH_2O_2 or CaO,H_2O, is soluble in water, but far less so than either the hydroxide of barium or of strontium, and, what is very remarkable, the *colder* the water, the larger is the quantity of the compound that is taken up. A pint of water at 15·5° dissolves about 11 grains, while at 100° only 7 grains are retained in solution. The hydroxide has

been obtained in thin delicate crystals by slow evaporation under the air-pump. Lime-water is always prepared for chemical and pharmaceutical purposes by agitating cold water with excess of calcium hydroxide in a closely-stopped vessel, and then, after subsidence, pouring off the clear liquid, and adding a fresh quantity of water, for another operation: there is not the least occasion for filtering the solution. Lime-water has a strong alkaline reaction, a nauseous taste, and when exposed to the air becomes almost instantly covered with a pellicle of carbonate, by absorption of carbonic acid. It is used, like baryta-water, as a test for carbonic acid, and in medicine. Lime-water prepared from some varieties of limestone may contain potash.

The hardening of mortars and cements is in a great measure due to the gradual absorption of carbonic acid; but even after a very great length of time, this conversion into carbonate is not complete. Mortar is known, under favourable circumstances, to acquire extreme hardness with age. Lime cements which resist the action of water contain iron oxides, silica, and alumina; they require to be carefully prepared, the stone not being over-heated. When they are ground to powder and mixed with water, solidification speedily ensues, from causes not yet thoroughly understood, and the cement, once in this condition, is unaffected by wet. Parker's or Roman cement is made in this manner from the nodular masses of calcareo-argillaceous ironstone found in the London clay.

Lime is of great importance in agriculture: it is found more or less in every fertile soil, and is often very advantageously added by the cultivator. The decay of vegetable fibre in the soil is thereby promoted, and other important objects, as the destruction of certain hurtful compounds of iron in marsh and peat land, are often attained. The addition of lime probably serves likewise to liberate potassium from the insoluble silicate of that base contained in the soil.

Calcium Dioxide, CaO_2, is obtained, in microscopic crystals, having the composition $CaO_2,8H_2O$, by precipitating lime-water with hydrogen dioxide.

Chloride of Lime, Bleaching Powder.—When calcium hydroxide, very slightly moist, is exposed to chlorine gas, the latter is absorbed, and a compound is produced—the bleaching powder of commerce—which is used on an immense scale for bleaching linen and cotton goods. At the commencement of the process, the chlorine must be supplied slowly, so as to avoid rise of temperature. The product when fresh and well prepared, is a soft white powder which attracts moisture slowly from the air, and exhales an odour sensibly different from that of chlorine. It is soluble in about 10 parts of water, the unaltered hydroxide being left behind: the solution is highly alkaline, and bleaches feebly. When calcium hydroxide is suspended in cold water, and chlorine gas transmitted through the mixture, the lime is gradually dissolved, and the same

peculiar bleaching compound produced; the alkalis also, either caustic or carbonated, may by similar means be made to absorb a large quantity of chlorine, and give rise to corresponding compounds: such are the "disinfecting solutions" of Labarraque.

The composition of bleaching powder is represented by the formula $CaOCl_2$, and it was formerly supposed to be a direct compound of lime with chlorine. This view, however, is not consistent with its reactions, for when distilled with dilute nitric acid, it readily yields a distillate of aqueous hypochlorous acid, and when treated with water it is resolved into chloride and hypochlorite of calcium, the latter of which may be separated in crystals by exposing the filtered solution to a freezing mixture, or by evaporating it in a vacuum over oil of vitriol, and leaving the dense frozen mass to thaw upon a filter. A solution of calcium chloride mixed with hypochlorite then passes through, and feathery crystals remain on the filter, very unstable, but consisting, when recently prepared, of hydrated calcium hypochlorite, $Ca(OCl)_2,4H_2O$.* These results seem at first sight to show that the bleaching powder is a mixture of chloride and hypochlorite of calcium, formed according to the equation,

$$2CaO + Cl_4 = CaCl_2 + CaCl_2O_2;$$

but if this were its true constitution, the powder when digested with alcohol, ought to yield a solution of calcium chloride containing half the chlorine of the original compound, which is not the case. Its constitution is therefore better represented by the formula Cl.Ca.OCl, suggested by Dr. Odling, this molecule being decomposed by water into chloride and hypochlorite in the manner just explained, and yielding, with dilute nitric or sulphuric acid, a distillate containing hydrochloric and hypochlorous acids:

$$CaCl(OCl) + 2HNO_3 = Ca(NO_3)_2 + HCl + HClO.$$

When the temperature of the calcium hydroxide has risen during the absorption of the chlorine, or when the compound has been subsequently exposed to heat, its bleaching properties are impaired or altogether destroyed: it then contains chlorate and chloride of calcium; oxygen, in variable quantity, is usually set free. The same change seems to ensue by long keeping, even at the common temperature of the air. In an open vessel the compound is speedily decomposed by the carbonic acid of the air. Commercial bleaching powder thus constantly varies in value with its age, and with the care originally bestowed upon its preparation: the best may contain about 30 per cent. of available chlorine, easily liberated by an acid, which is, however, far short of the theoretical quantity.

The general method in which this substance is employed for bleaching is the following:—The goods are first immersed in a dilute solution of chloride of lime, and then transferred to a vat con-

* Kingzett, Chem. Soc. Jour., 1875, p. 404.

taining dilute sulphuric acid. Decomposition ensues; the calcium both of the hypochlorite and of the chloride is converted into sulphate, while the free hypochlorous and hydrochloric acids yield water and free chlorine:—

$$CaOCl_2 + H_2SO_4 = CaSO_4 + HClO + HCl, \text{ and}$$
$$HClO + HCl = H_2O + Cl_2.$$

The chlorine thus disengaged in contact with the cloth causes destruction of the colouring matter. The process is repeated several times, since it is unsafe to use strong solutions.

On the same principle, white patterns are imprinted upon coloured cloth, the figures being stamped with tartaric acid thickened with gum-water, and then the stuff immersed in the chlorine bath, when the parts to which no acid has been applied remain unaltered, while the printed portions are bleached.

For purifying an offensive or infectious atmosphere, *as an aid to proper ventilation*, the bleaching powder is very convenient. The solution is exposed in shallow vessels, or cloths steeped in it are suspended in the apartment, when the carbonic acid of the air slowly decomposes it in the manner above described. Addition of a strong acid causes rapid disengagement of chlorine.

The value of any sample of bleaching powder may be easily determined by the following method, in which the feebly combined chlorine is estimated by its effect in oxidising a ferrous salt to ferric salt, 2 molecules of ferrous oxide, FeO, requiring for the purpose 2 atoms of chlorine, according to the equation: $2FeSO_4 + H_2SO_4 + Cl_2 = 2HCl + Fe_2(SO_4)_3$. To make the estimation, 0·784 gram of pure crystallised ferrous sulphate is dissolved in water, a little sulphuric acid is added, and the solution of bleaching powder is dropped in from a burette till all the ferrous salt is converted into ferric salt. The completion of the reaction is ascertained by bringing a drop of the solution, together with a drop of potassium ferricyanide, on a white plate, until no further coloration is observed. A simple calculation gives the result, the above quantity of ferrous sulphate, $FeSO_4,7H_2O$, being equivalent to 1 gram of chlorine.

Calcium Sulphate, $CaSO_4$.—Crystalline native calcium sulphate, containing 2 molecules of water, is found in considerable abundance in some localities as *gypsum:* it is often associated with rock-salt. When regularly crystallised, it is termed *selenite*. Anhydrous calcium sulphate is also occasionally met with. The salt is formed by precipitation, when a moderately concentrated solution of calcium chloride is mixed with sulphuric acid. Calcium sulphate is soluble in about 500 parts of cold water, and its solubility is a little increased by heat. It is more soluble in water containing ammonium chloride or potassium nitrate. The solution is precipitated by alcohol. Gypsum, or native hydrated calcium sulphate, is largely employed for the purpose of making casts of statues and medals, also for

moulds in the porcelain and earthenware manufactures, and for other applications. It is exposed to heat in an oven where the temperature does not exceed 127°, by which the water of crystallisation is expelled, and it is afterwards reduced to a fine powder. When mixed with water, it solidifies after a short time, from the re-formation of the same hydrate; but this effect does not happen if the gypsum has been over-heated. It is often called Plaster of Paris. Artificial coloured marbles, or *scagliola*, are frequently prepared by inserting pieces of natural stone in a soft stucco containing this substance, and polishing the surface when the cement has become hard. Calcium sulphate is one of the most common impurities of spring water.

The peculiar property water acquires by the presence of calcium salts is termed *hardness*. It manifests itself by the effect such waters have upon the palate, and particularly by its peculiar behaviour with soap. Hard water yields a lather with soap only after the whole of the calcium salts have been thrown down from the water in the form of an insoluble lime-soap. The hardness produced by calcium sulphate is called *permanent hardness*, since it cannot be remedied.

Calcium and Potassium Sulphate, $CaSO_4,K_2SO_4 + H_2O$, is formed by the solutions of the two salts mixed together. An intimate mixture of equal weights of the anhydrous salts, stirred up with less than their weight of water, coagulates suddenly to a solid mass. With 4 to 5 parts of water, solidification takes place more slowly, and the mixture may be used for taking casts.—*Calcium and Sodium Sulphate*, $CaSO_4,Na_2SO_4$, occurs native as *Glauberite*. Needle-shaped crystals, having the composition $CaSO_4,Na_2SO_4,2H_2O$ are obtained on mixing 1 part precipitated calcium sulphate and 50 parts Glauber's salt, and heating the mixture at 80° with 25 parts water. When further heated, they are transformed into small crystals of glauberite.

Calcium Nitrate, $Ca(NO_3)_2$.—This salt, prepared by dissolving chalk in nitric acid, is in the anhydrous state a white porous deliquescent mass, very soluble in water and in alcohol. When heated and then exposed to sunshine, it appears luminous in the dark, and is hence called "Baldwin's Phosphorus," from the name of the alchemist Baldewein or Balduinus, who first prepared it. It is often found as an efflorescence on the walls of stables and other places through which urine or other organic liquids percolate: hence it has been called *lime-saltpetre* or *wall-saltpetre*.

Calcium Phosphates.—The *tricalcic salt*, $Ca_3(PO_4)_2$ or $3CaO,P_2O_5$, occurs, combined with chloride and fluoride of calcium, in apatite, which crystallises in the rhombohedral system; and its massive varieties, *phosphorite* and *estremadurite*, which occur in Estremadura in Spain, have the composition $3Ca_3(PO_4)_2 + CaF_2$, the fluorine being sometimes partly replaced by chlorine. Tricalcic *phosphate* occurs pure in osteolite, a mineral found near Hanau

and at Amberg in the Erzgebirge; also pure in ornithite, a crystallised mineral found in the guano of Sombrero, a small island of the Antilles group; and mixed with an aluminium phosphate in sombrerite, occurring also in the same islands. Tricalcic phosphate is also the chief mineral constituent of bones, in the ash of which it occurs to the amount of about 80 per cent., together with magnesium phosphate, calcium carbonate, and calcium fluoride.

Tricalcic phosphate is obtained as a white precipitate by adding disodic orthophosphate (ordinary phosphate of soda) to an ammoniacal solution of calcium chloride. It is nearly insoluble in water, but is decomposed by prolonged boiling with water into an insoluble basic salt, $Ca_3(PO_4)_2 + Ca_2(PO_4)OH$, and a soluble acid salt. It dissolves also in water containing ammoniacal salts, chloride and nitrate of sodium, and other salts; easily also in all acids, even in aqueous carbonic acid.

Monocalcic Orthophosphate, $CaHPO_4$, separates with 2 mols. H_2O, as a white crystalline precipitate, on treating a solution of calcium chloride with ordinary sodium phosphate. It occurs in urinary concretions, and is sometimes deposited from urine in rosettes or stellate groups of microscopic crystals.

Tetrahydro-calcic Phosphate, $H_4Ca(PO_4)_2$, separates in rhombic tablets, when a solution of either of the preceding salts in the requisite quantity of phosphoric acid is left to evaporate. By treatment with boiling water, it is converted into the anhydrous monocalcic salt, and with cold water into the same with $2H_2O$.

Superphosphate of Lime.—This name is applied to a mixture of monocalcic orthophosphate and calcium sulphate prepared on the large scale by treating bone-ash, coprolites, phosphorites, &c., with two-thirds of their weight of sulphuric acid. It is used for the preparation of phosphorus, and very largely as a manure, especially for root-crops.

Calcium Hypophosphite, $Ca(PO_2H_2)_2$, a salt used in medicine, is prepared by boiling phosphorus with milk of lime, and separates from the clear solution on evaporation in bright flexible four-sided prisms, insoluble in alcohol.

Calcium Carbonate, *Chalk; Limestone; Marble;* $CaCO_3$.—Calcium carbonate, often more or less contaminated with iron oxide, clay, and organic matter, forms rocky beds, of immense extent and thickness, in almost every part of the world. These present the greatest diversities of texture and appearance, arising, in a great measure, from changes to which they have been subjected since their deposition. The most ancient and highly crystalline limestones are destitute of visible organic remains, while those of more recent origin are often entirely made up of the shelly exuviæ of once-living beings. Sometimes these latter are of such a nature as to show that the animals inhabited fresh water; marine species and corals are, however, most abundant. Cavities in limestone and other rocks are very often lined with magnificent crystals of calcium

carbonate or calcareous spar, which have evidently been slowly deposited from a watery solution. Calcium carbonate is always precipitated when an alkaline carbonate is mixed with a solution of that base.

Although this substance is not sensibly soluble in pure water, it is freely taken up when carbonic acid happens at the same time to be present. If a little lime-water be poured into a vessel of that gas, the turbidity first produced disappears on agitation, and a transparent solution of calcium carbonate in excess of carbonic acid is obtained. This solution is decomposed completely by boiling, the carbonic acid being expelled, and the carbonate precipitated. Since all natural waters contain dissolved carbonic acid, it is to be expected that calcium in this state should be of very common occurrence; and such is really found to be the fact, river, and more especially spring water, almost invariably containing calcium carbonate thus dissolved. In limestone districts, this is often the case to a great extent. The *hardness* of water due to the presence of calcium carbonate, is called *temporary*, since it is diminished to a very considerable extent by boiling, and may be nearly removed by mixing the hard water with lime-water, when both the dissolved carbonate and the dissolved lime, which thus becomes carbonated, are precipitated. Upon this principle Dr. Clark's process of softening water is based. This process is of considerable importance, since a supply of hard water to towns is in many respects a source of great inconvenience. As already mentioned, the use of such water, for the purposes of washing, is attended with a great loss of soap. Boilers, in which such water is heated, speedily become lined with a thick stony incrustation.* The beautiful stalactitic incrustations of limestone caverns, and the deposit of calc sinter or travertin upon various objects, and upon the ground, in many places, are explained by the solubility of calcium carbonate in water containing carbonic acid.

Crystallised calcium carbonate is dimorphous; calc-spar and arragonite, although possessing exactly the same chemical composition, have different crystalline forms, different densities, and different optical properties. Rose has observed that calcium carbonate appears in the form of calc-spar when deposited from its solution in water containing carbonic acid at the ordinary temperature. At 90°, however, and at the boiling heat, it is chiefly deposited in the form of arragonite; at lower temperatures the formation of arra-

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* Many proposals have been made to prevent the formation of boiler deposits. The most efficient appears to be the method of Dr. Ritterband, which consists in throwing into the boiler a small quantity of sal-ammoniac, whereby carbonate of ammonia is formed, which is volatilised with the steam, calcium chloride remaining in solution. It need scarcely be mentioned that this plan is inapplicable in the case of permanently hard *waters*.

gonite decreases, whilst that of calc-spar increases, the limit for the formation of the former variety being between 30° and 50°.

Calc-spar occurs very abundantly in crystals derived from an obtuse rhombohedron, whose angles measure 105° 5′ and 74° 55′ : its density varies from 2·5 to 2·8. The rarer variety, or arragonite, is found in crystals whose primary form is a right rhombic prism, a figure having no geometrical relation to the preceding : it is, besides, heavier and harder. Sp. gr. = 2·92 to 3·28.

Calcium Sulphides.—The monosulphide, CaS, is obtained by reducing the sulphate at a high temperature with charcoal or hydrogen : it is nearly colourless, and but little soluble in water. By boiling together calcium hydrate, water, and flowers of sulphur, a red solution is obtained, which, on cooling, deposits crystals of the bisulphide, CaS_2, containing water. When the sulphur is in excess, and the boiling long continued, a pentasulphide is generated : thiosulphuric acid is also formed during these reactions :

$$3CaO + S_6 = 2CaS_2 + CaS_2O_3.$$

When the yellow solution obtained by boiling lime with excess of sulphur is poured into an excess of hydrochloric acid, sulphur is precipitated together with a yellow oily liquid, which is hydrogen persulphide (p. 187) ; but if the acid be poured into the solution of calcium sulphide, gaseous hydrogen sulphide is given off, and the whole precipitate formed consists wholly of finely-divided sulphur, the *sulphur precipitatum* of the Pharmacopœia. If dilute sulphuric acid is used, the precipitate also contains gypsum.

Calcium Phosphide.—When vapour of phosphorus is passed over fragments of lime heated to redness in a porcelain crucible, a chocolate-brown compound, the so-called *phosphuret of lime*, is produced. This substance is probably a mixture of calcium phosphide and phosphate. When thrown into water, it yields spontaneously inflammable hydrogen phosphide. According to Paul Thénard, the calcium phosphide in this compound has the composition P_2Ca_2. In contact with water it yields liquid hydrogen phosphide, P_2H_4 (p. 228).

$$P_2Ca_2 + 2H_2O = 2CaO + P_2H_4 :$$

and the greater portion of this liquid phosphide is immediately decomposed into solid and gaseous hydrogen phosphide : $5P_2H_4 = P_4H_2 + 6PH_3$.

Respecting the reactions of calcium salts, see page 412.

STRONTIUM.

Symbol, Sr. Atomic weight, 87·2.

THIS element occurs as carbonate in the mineral called *Strontianite*, found at Strontian, in Argyleshire, also as sulphate or *Cœlestin;* in small quantity, as chloride or sulphate in many brine-springs and mineral waters, in sea-water, and in the ash of *Fucus vesiculosus*.

Metallic strontium was discovered by Davy, who obtained it by electrolysis of the moistened peroxide or of the aqueous chloride, but it is more readily prepared by electrolysis of the fused anhydrous chloride. A small porcelain crucible having a porous cell is filled with strontium chloride mixed with a little sal-ammoniac; a fine iron wire placed within the cell constitutes the negative pole, and the positive pole is an iron cylinder placed in the crucible round the cell. The heat is regulated so that a crust forms in the cell, and the metal collects under this crust (Matthiessen).

Strontium is a yellow metal, somewhat harder than calcium, malleable, and having a density of 2·5. It melts at a red heat, and is more electronegative than calcium or the alkali-metals. It oxidises quickly in the air, burns brilliantly when heated, and decomposes water at common temperatures.

Strontium Chloride, $SrCl_2$, prepared by dissolving the carbonate in hydrochloric acid, crystallises in colourless needles or prisms, $SrCl_2,6H_2O$, which are slightly deliquescent, dissolve in 2 parts of cold and a smaller quantity of boiling water; also in alcohol, forming a solution which burns with a crimson flame.

Oxides.—The *monoxide* or *Strontia*, prepared by ignition of the nitrate, is a greyish-white porous infusible mass. It unites readily with a small quantity of water, forming a white powder of strontium hydroxide, $Sr(OH)_2$, which dissolves readily in hot water, and separates on cooling as a hydrate, $Sr(OH)_2,8H_2O$, soluble in 50 parts of cold, and 2·4 of boiling water. The solution is alkaline and caustic, but less so than those of the alkalis or of baryta.—The *dioxide*, SrO_2, is prepared by the action of hydrogen dioxide on strontia-water, and separates in pearly scales containing 2 molecules of water, which they give off when heated.

Strontium Sulphate, $SrSO_4$, occurs native in rhombic crystals and fibrous masses having a light blue colour: hence called *cœlestin*. The same compound is thrown down as a white precipitate, of sp. gr. 3·707, when sulphuric acid or a soluble sulphate is added to a solution of a strontium salt. It is intermediate in solubility between the sulphates of calcium and barium, and less soluble in boiling than in cold water.

Strontium Nitrate, $Sr(NO_3)_2$, crystallises in anhydrous octo-

hedrons, soluble in 5 parts of cold, and about half their weight of boiling water. It is chiefly of value to the pyrotechnist, who employs it in the composition of the well known "red fire."*

Strontium Carbonate, $SrCO_3$, occurs as strontianite in crystals isomorphous with those of arragonite, and is obtained by precipitation as a white impalpable powder, having a density of 3·62. When boiled with sal-ammoniac, it is converted into the chloride.

All strontium compounds impart a deep crimson colour to the flame of alcohol. Their spectral reactions have been already noticed (p. 89). For their reactions with liquid reagents, see page 412.

BARIUM.†

Symbol, Ba. Atomic weight, 136·8.

THIS metal occurs abundantly as sulphate and carbonate, forming the *veinstone* in many lead mines. Davy obtained it in the metallic state by means similar to those described in the case of lithium. Bunsen subjects barium chloride mixed to a paste with water and a little hydrochloric acid, at a temperature of 100°, to the action of the electric current, using an amalgamated platinum wire as the negative pole. In this manner the metal is obtained as a solid, highly crystalline amalgam, which, when heated in a stream of hydrogen, yields barium in the form of a tumefied mass, tarnished on the surface, but often exhibiting a silver-white lustre in the cavities. Barium may also be obtained, though impure, by passing vapour of potassium over the red-hot chloride or oxide of barium. It is malleable, melts below a red heat, decomposes water, and gradually oxidises in the air.

Barium Chloride, $BaCl_2,2H_2O$, is prepared by dissolving the native carbonate in hydrochloric acid, filtering the solution, and eva-

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* RED FIRE:

	Grains.
Dry strontium nitrate	800
Sulphur	225
Potassium chlorate	200
Lampblack	50

GREEN FIRE:

	Grains.
Dry barium nitrate	450
Sulphur	150
Potassium chlorate	100
Lampblack	25

The strontium or barium-salt, the sulphur, and the lampblack must be finely powdered and intimately mixed, after which the potassium chlorate should be added in rather coarse powder, without rubbing, with the other ingredients. The red fire composition has been known to ignite spontaneously.

† From *βαρύς*, heavy, in allusion to the great specific gravity of the native carbonate and sulphate.

however, sal-ammoniac, potassium chloride, or sodium chloride is present, a double salt is produced, which is easily rendered anhydrous. The best mode of preparing the chloride is to divide a quantity of hydrochloric acid into two equal portions, to neutralise one with magnesia, and the other with ammonia, or carbonate of ammonia; to mix these solutions, evaporate them to dryness, and then expose the salt to a red heat in a loosely covered porcelain crucible. Sal-ammoniac sublimes, and fused magnesium chloride remains; the latter is poured out upon a clean stone, and when cold transferred to a well-stopped bottle.

The chloride so obtained is white and crystalline. It is very deliquescent and highly soluble in water, from which it cannot again be recovered by evaporation, for the reasons just mentioned. When long exposed to the air in the melted state, it is converted into magnesia. It is soluble in alcohol.

Magnesium chloride occurs in sea-water, in many brine-springs and salt-beds, and is prepared in large quantities at Stassfurt.

Magnesium Oxide, or **Magnesia**, MgO, is easily prepared by exposing the *magnesia alba* of pharmacy, which is a hydrocarbonate, to a full red heat in an earthen or platinum crucible. It forms a soft, white powder, which slowly attracts moisture and carbonic acid from the air, and unites quietly with water to a slightly soluble hydrate requiring for solution about 5000 parts of water at 15·5° and 36,000 parts at 100°. The alkalinity of magnesia can be observed only by placing a small portion in the moist state upon test-paper; but it neutralises acids completely. It is infusible.

Magnesium sulphide is formed by passing vapour of carbon sulphide over magnesia, in capsules of coke, at a strong red heat.

Oxysalts of Magnesium—The *Sulphate*, $MgSO_4,7H_2O$, commonly called Epsom salt, occurs in sea-water, and in many mineral springs, and is now manufactured in large quantities by acting on magnesian limestone with dilute sulphuric acid, and separating the magnesium sulphate from the greater part of the slightly soluble calcium sulphate by filtration. The crystals are derived from a right rhombic prism; they are soluble in an equal weight of water at 5·5°, and in a still smaller quantity at 100°. The salt has a nauseous bitter taste, and, like many other neutral salts, possesses purgative properties. When it is exposed to heat, 6 molecules of water readily pass off, the seventh being energetically retained. Magnesium sulphate forms with the sulphates of potassium and ammonium, beautiful double salts which contain 6 molecules of crystallisation-water, their formulæ being $MgK_2(SO_4)_2,6H_2O$, and $Mg(NH_4)_2(SO_4)_2,6H_2O$. These salts are isomorphous, and form monoclinic crystals.

Magnesium Phosphate, $MgHPO_4,7H_2O$, separates in small colourless prismatic crystals when solutions of sodium phosphate and

magnesium sulphate are mixed and left at rest for some time. According to Graham, it is soluble in about 1000 parts of cold water. Magnesium phosphate exists in the grain of the cereals, and can be detected in considerable quantity in beer.

Magnesium and Ammonium Phosphate, $Mg(NH_4)PO_4,6H_2O$.—When ammonia or its carbonate is mixed with a magnesium salt, and a soluble phosphate is added, a crystalline precipitate having the above composition, subsides, immediately if the solutions are concentrated, and after some time if they are very dilute: in the latter case, the precipitation is promoted by stirring. This salt is slightly soluble in pure water, but nearly insoluble in saline and ammoniacal liquids. When heated, it gives off water and ammonia, and is converted into *magnesium pyrophosphate*, $Mg_2P_2O_7$:

$$2Mg(NH_4)PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3.$$

At a strong red heat it fuses to a white enamel-like mass. Magnesium and ammonium phosphate sometimes forms a urinary calculus, and occurs also in guano.

In analysis, magnesium is often separated from solutions by bringing it into this state. The liquid, free from alumina, lime, &c., is mixed with sodium phosphate and excess of ammonia, and gently heated for a short time. The precipitate is collected upon a filter and thoroughly washed with water containing a little ammonia, after which it is dried, ignited to redness, and weighed. The proportion of magnesia is then easily calculated.

Silicates.—The following natural compounds belong to this class: *Chrysolite*, $Mg_2SiO_4 = 2MgO,SiO_2$, a crystallised mineral, sometimes employed for ornamental purposes: a portion of the magnesia is commonly replaced by ferrous oxide, which communicates a green colour. *Meerschaum*, $2MgSiO_3,SiO_2 = 2MgO,3SiO_2$, is a soft sectile mineral, from which pipe-bowls are made. *Talc*, $4MgSiO_3,SiO_2,4H_2O$ (called *steatite* when massive), is a soft, white, sectile, transparent or translucent mineral, used as firestones for furnaces and stoves, and in thin plates for glazing lanthorns, &c.; also in the state of powder for diminishing friction. *Soapstone*, also called steatite, is a silicate of magnesium and aluminium of somewhat variable composition. *Serpentine* is a combination of silicate and hydroxide of magnesium. *Jade*, an exceedingly hard stone, brought from New Zealand, is a silicate of magnesium and aluminium: its green colour is due to chromium. *Augite* and *hornblende* are essentially double silicates of magnesia and lime, in which the magnesia is more or less replaced by its isomorphous substitute, ferrous oxide.

Carbonates.—The *normal carbonate*, $MgCO_3$ or MgO,CO_2, occurs native in rhombohedral crystals, resembling those of calc-spar, imbedded in talc-slate: a soft earthy variety is sometimes met with.

When magnesia alba is dissolved in aqueous carbonic acid, and the solution left to evaporate spontaneously, small prismatic crystals

are deposited, consisting of trihydrated magnesium carbonate, $MgCO_3,3H_2O$.

The magnesia alba itself, although often called carbonate of magnesium, is not so in reality; it is a compound of carbonate with hydroxide. It is prepared by mixing hot solutions of potassium or sodium carbonate and magnesium sulphate, the latter being kept in slight excess, boiling the whole for a few minutes, during which time much carbonic acid is disengaged, and well washing the precipitate so produced. If the solution is very dilute, the magnesia alba is exceedingly light and bulky; if otherwise, it is denser. The composition of this precipitate is not perfectly constant. In most cases it contains $4MgCO_3,MgH_2O_2,6H_2O$.

Magnesia alba is slightly soluble in water, especially when cold.

Magnesium salts are isomorphous with zinc salts, ferrous salts, cupric salts, cobalt salts, and nickel salts, &c.; they are usually colourless, and are easily recognised by the following characters:—A gelatinous white precipitate with *caustic alkalis*, including *ammonia*, insoluble in excess, but soluble in solution of sal-ammoniac. A white precipitate with *potassium* and *sodium carbonates*, but none with ammonium carbonate in the cold. A white crystalline precipitate with soluble *phosphates*, on the addition of a little ammonia.

ZINC.

Symbol, Zn. Atomic weight, 64·9.

Zinc is a somewhat abundant metal: it is found in the state of carbonate, silicate, and sulphide, associated with lead ores in many districts, both in Britain and on the Continent; large supplies are obtained from Silesia, and from the neighbourhood of Aachen. The native carbonate, or *calamine*, is the most valuable of the zinc ores, and is preferred for the extraction of the metal: it is first roasted to expel water and carbonic acid, then mixed with fragments of coke or charcoal, and distilled at a full red heat in a large earthen retort; carbon monoxide then escapes, while the reduced metal volatilises and is condensed by suitable means, generally with minute quantities of arsenic.

Zinc is a bluish-white metal, which slowly tarnishes in the air: it has a lamellar, crystalline structure, a density varying from 6·8 to 7·8, and is, under ordinary circumstances, brittle. Between 120° and 150° it is, on the contrary, malleable, and may be rolled or hammered without danger of fracture; and, what is very remarkable, after such treatment, it retains its malleability when cold; the sheet-zinc of commerce is thus made. At 210° it is so brittle that it may

be reduced to powder. It melts at 412°; boils at 930° (Violle), 932° (Becquerel), 1040° (Deville and Troost), and, if air be admitted, burns with a splendid greenish light, generating the oxide. Dilute acids dissolve zinc very readily: it is constantly employed in this manner for preparing hydrogen gas.

Zinc chloride, $ZnCl_2$, may be prepared by heating metallic zinc in chlorine: by distilling a mixture of zinc-filings and corrosive sublimate; or, more easily, by dissolving zinc in hydrochloric acid. It is a nearly white, translucent, fusible substance, very soluble in water and alcohol, and very deliquescent. A strong solution of zinc chloride is sometimes used as a bath for obtaining a graduated heat above 100°. Zinc chloride unites with sal-ammoniac and potassium chloride to form double salts: the former of these, made by dissolving zinc in hydrochloric acid, and then adding an equivalent quantity of sal-ammoniac, is very useful in tinning and soft-soldering copper and iron.

The *oxide*, ZnO, is a strong base, forming salts isomorphous with the magnesium salts. It is prepared either by burning zinc in atmospheric air, or by heating the carbonate to redness. Zinc oxide is a white, tasteless powder, insoluble in water, but freely dissolved by acids. When heated it is yellow, but turns white again on cooling. It is sometimes used as a substitute for white lead. To prepare zinc-white on a large scale, metallic zinc is volatilised in large earthen muffles, whence the zinc vapour passes into a small receiver (*guérite*), where it comes in contact with a current of air and is oxidised. The zinc oxide thus formed passes immediately into a condensing chamber divided into several compartments by cloths suspended within it.

The *sulphate*, $ZnSO_4,7H_2O$, commonly called *White Vitriol*, is hardly to be distinguished by the eye from magnesium sulphate: it is prepared either by dissolving the metal in dilute sulphuric acid, or, more economically, by roasting the native sulphide, or *blende*, which, by absorption of oxygen, becomes in great part converted into sulphate. The altered mineral is thrown hot into water, and the salt is obtained by evaporating the clear solution. Zinc sulphate has an astringent metallic taste, and is used in medicine as an emetic. The crystals dissolve in $2\frac{1}{2}$ parts of cold, and in a much smaller quantity of hot water. Crystals containing 6 molecules of water have been observed. Zinc sulphate forms double salts with the sulphates of potassium and ammonium, namely, $ZnK_2(SO_4)_2,6H_2O$ and $Zn(NH_4)_2,6H_2O$, isomorphous with the corresponding magnesium salts.

The *carbonate*, $ZnCO_3$, is found native; the white precipitate obtained by mixing solutions of zinc and of alkaline carbonates, is a combination of carbonate and hydroxide. When heated to redness, it yields pure zinc oxide.

The *sulphide*, ZnS, occurs native, as *blende*, in regular tetrahedrons, dodecahedrons, and other monometric forms, and of various colours, from white or yellow to brown or black, according to its

METALS OF THE LEAD GROUP.

Lead—Thallium.

THESE metals are soft, heavy, and form basic oxides having an alkaline reaction. Thallium in many of its properties closely resembles the alkali-metals, and lead resembles the metals of the alkaline earths in forming an insoluble carbonate and sulphate; but lead and thallium are distinguished from both these groups by the black colour and insolubility of their sulphides, and the sparing solubility of their dichlorides.

LEAD.

Symbol, Pb (Plumbum). Atomic weight, 206·4.

THIS abundant and useful metal is wholly obtained from the native sulphide, or *galena*, no other lead-ore being found in large quantity. The reduction is effected in a reverberatory furnace, into which the crushed lead-ore is introduced and roasted for some time at a dull red heat, by which much of the sulphide is oxidised to sulphate. The contents of the furnace are then thoroughly mixed, and the temperature raised, whereupon the sulphate and oxide react with the remaining sulphide in such a manner as to produce sulphur dioxide and metallic lead:

$$2PbO + PbS = SO_2 + 3Pb$$
$$\text{and } PbSO_4 + PbS = 2SO_2 + 2Pb.$$

The lead thus produced sometimes contains antimony and other metals, which render it hard. They may, however, be removed, and the lead rendered soft by melting and partially oxidising it in a reverberatory furnace with a cast-iron bottom. The lead so far purified still contains silver in sufficient quantity to render it worth extracting; in fact a considerable proportion of the silver which now comes into the market is obtained from argentiferous galena. The method of separating the silver will be described under SILVER.

Lead is a soft bluish metal, possessing very little elasticity; its specific gravity is 11·45. It may be easily rolled out into plates, or drawn out into coarse wires, but has very little tenacity. It melts at 315·5°, or a little above, and boils and volatilises at a white heat. By slow cooling, it may be obtained in octohedral crystals. In moist air it becomes coated with a film of grey matter, thought to be suboxide, and when exposed to the atmosphere in the melted

state it rapidly absorbs oxygen. Dilute acids, with the exception of nitric acid, act but slowly upon lead.

Lead is a tetrad, as shown by the composition of plumbic ethide, $Pb(C_2H_5)_4$, and of the perchloride, probably, $PbCl_4$, and the peroxide PbO_2. In the greater number of its compounds, however, it is bivalent, as in the dichloride $PbCl_2$, the corresponding bromide and iodide, and the monoxide PbO.

Chlorides.—The *dichloride*, $PbCl_2$, is prepared by precipitating a solution of lead nitrate or acetate with hydrochloric acid or common salt, and separates as a heavy white crystalline precipitate, which dissolves in about 33 parts of boiling water, and separates again, on cooling, in needle-shaped crystals.

The *perchloride*, probably, $PbCl_4$, is obtained by dissolving the dioxide in strong well-cooled hydrochloric acid, whereby a yellow, strongly oxidising solution is obtained, from which water and alkalis throw down the dioxide.

Oxychlorides.—The compound $Pb_3Cl_2O_2$ or $PbCl_2,2PbO$ occurs crystallised in rhombic prisms on the Mendip Hills, and is thence called *Mendipite*. Another oxychloride, constituting Pattinson's white oxychloride, Pb_2Cl_2O or $PbCl_2,PbO$, is prepared for use as a pigment by grinding galena with strong hydrochloric acid, dissolving the resulting chloride in hot water, and precipitating with lime-water. A third oxychloride, $PbCl_2,7PbO$, called *Patent yellow* or *Turner's yellow*, is prepared by heating 1 part of sal-ammoniac with 13 parts of litharge.

Lead Iodide, PbI_2, is precipitated, on mixing the nitrate or acetate with potassium iodide, as a bright yellow powder, which dissolves in boiling water, and crystallises therefrom in beautiful yellow iridescent spangles.

Oxides.—*Diplumbic oxide*, or *Lead suboxide*, Pb_2O, is formed when the monoxide is heated to dull redness in a retort: a grey pulverulent substance is then left, which is resolved by acids into monoxide and metal. It absorbs oxygen with great rapidity when heated, and even when simply moistened with water and exposed to the air.

The *monoxide*, PbO, called *Litharge* or *Massicot*, is the product of the direct oxidation of the metal. It is most conveniently prepared by heating the carbonate to dull redness; common *litharge* is impure monoxide which has undergone fusion. Lead oxide has a delicate straw-yellow colour, is very heavy, and slightly soluble in water, giving an alkaline liquid. It is soluble in potash, and crystallises from the solution in rhombic prisms. At a red heat it melts, and tends to crystallise on cooling. In the melted state it attacks and dissolves siliceous matter with astonishing facility, often penetrating an earthen crucible in a few minutes. It is easily reduced when heated with organic substances of any kind contain-

ing carbon or hydrogen. It forms a large class of salts, often called *plumbic salts*, which are colourless if the acid itself is not coloured.

A *basic hydroxide*, $Pb_2O(OH)_2$ or HO.Pb.O.Pb.OH, is obtained as a white precipitate by the action of air and water free from carbonic acid on metallic lead, and is thrown down as a white precipitate on addition of ammonia or a fixed alkali to a lead salt, the precipitate in the latter case being redissolved by excess of the reagent. The hydroxide gives off part of its water at 130°, and the whole at 145°. Both the hydroxide and the oxide are somewhat soluble in water, and turn reddened litmus-paper blue. They act as strong bases and also as acids, combining with certain metallic oxides, the lead oxide when fused with these bases forming a glass.

The *sesquioxide*, Pb_2O_3, is formed by the action of sodium hypochlorite on a solution of the monoxide in potash, and when a solution of red lead in acetic acid is precipitated by very dilute ammonia. The reddish-yellow powder thus formed contains water, part of which it retains even at 150°. It is resolved by acids into PbO and PbO_2.

Triplumbic tetroxide, or *Red lead*, is not of very constant composition, but generally contains Pb_3O_4 or $2PbO,PbO_2$. It is prepared by exposing the monoxide, which has not been fused, for a long time to the air, at a very faint red heat. It is a brilliant red and extremely heavy powder, decomposed, with evolution of oxygen, by a strong heat, and converted by acids into a mixture of monoxide and dioxide. It is used as a cheap substitute for vermillion.

The *dioxide*, PbO_2, often called *Puce* or *Brown lead-oxide*, is easily obtained by digesting red lead in dilute nitric acid, whereby lead nitrate is dissolved out, and insoluble dioxide left behind in the form of a deep-brown powder. It is also formed by the action of chlorine on lead-salts in presence of alkalis, and, as already observed (p. 316), by the electrolysis of lead salts, being deposited on the anode. The dioxide is decomposed by a red heat, yielding up one-half of its oxygen. By hydrochloric acid it is converted into lead chloride, with disengagement of chlorine, and by hot sulphuric acid into sulphate, with liberation of oxygen. The dioxide is very useful in separating sulphurous oxide from certain gaseous mixtures, lead sulphate being then produced: $PbO_2 + SO_2 = PbSO_4$. The dioxide possesses acid properties. When fused in a silver crucible with excess of potassium hydroxide, it yields crystalline *potassium plumbate*, $K_2PbO_3,2H_2O$, the solution of which gives with most metallic salts precipitates of the corresponding plumbates.

Lead Sulphate, $PbSO_4$, occurs native as *Lead-vitriol* or *Anglesite* in transparent rhombic crystals isomorphous with cælestin, $SrSO_4$, and heavy spar, $BaSO_4$, and is obtained as a white powder soluble in alkalis, by precipitating a lead salt with sulphuric acid or a soluble sulphate.

Lead Nitrate, $Pb(NO_3)_2$, or PbO,N_2O_5, may be obtained by dissolving lead carbonate in nitric acid, or by acting directly upon the metal with the same agent aided by heat: it is, as already noticed, a bye-product in the preparation of the dioxide. It crystallises in anhydrous octohedrons, which are usually milk-white and opaque. It dissolves in $7\frac{1}{2}$ parts of cold water, and is decomposed by heat, yielding nitrogen tetroxide, oxygen, and lead monoxide, which obstinately retains traces of nitrogen. When a solution of this salt is boiled with an additional quantity of lead oxide, a portion of the latter is dissolved, and a basic nitrate generated, which may be obtained in crystals. Carbonic acid separates this excess of oxide in the form of a white compound of carbonate and hydrate of lead.

By boiling a solution of lead nitrate for several hours with lead-turnings, N. v. Lorenz* has lately obtained a number of basic nitrates and nitrites of lead, the composition of which is shown in the following table, from which it will be seen that, as the action progresses, the amounts of nitrite and oxide or hydroxide in the salts produced increases continually in proportion to the nitrate. The symbol A stands for the basic nitrate, $NO_3.Pb.OH$, and B for the nitrite, $NO_2.Pb.OH$:

$NO_3.Pb.OH$	
$3(2A + B) + H_2O$	$4A + 6B + 5PbO + Pb(OH)_2$
$3(A + B) + 2H_2O$	$2A + 4B + 3PbO + Pb(OH)_2$
$6A + 7B + 4H_2O$	$Pb(NO_3)_2 + 2PbO$ or
$3A + 5B + H_2O$	$5Pb(NO_2)_2 + NO_3.Pb.OH + 10PbO$
$3A + 6B + H_2O$	$NO_2.Pb.OH + PbO$
$3A + 9B + H_2O$	
$A + 4B$	
$A + 5B$	

Respecting the mode of formation and the physical characters of these successive products, reference must be made to the paper above cited.

Lead Phosphates.—The *Normal Orthophosphate*, $Pb_3(PO_4)_2$, is obtained as a white precipitate on adding ordinary phosphate of soda to a solution of lead acetate. A boiling solution of lead nitrate mixed with phosphoric acid yields a glittering white crystalline precipitate of an acid phosphate, $HPbPO_4$. A phosphato-chloride of lead, $Pb_3PO_4,Pb_2(PO_4)Cl$, occurs native as *pyromorphite*, and the corresponding arsenato-chloride as *mimetesite*. In both these minerals a portion of the chlorine is usually replaced by fluorine.

Lead Silicates.—Silica fuses with lead oxide to a yellow glass. Lead silicate forms a constituent of flint glass.

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* Monatshefte für Chemie, 1881, pp. 810—841, and Journal of the Chemical Society, 1882, vol. xlii. p. 364.

Lead Carbonates.—The *normal salt*, $PbCO_3$, occurs native as *cerusite* in white rhombic crystals isomorphous with arragonite; also in pseudomorphs after galena and lead sulphate. The same compound is formed by precipitating a cold solution of lead acetate with carbonate of ammonia, and by passing carbon dioxide into a dilute solution of normal lead acetate.

Lead forms several basic carbonates, the most important of which, known as *White Lead*, is manufactured on a very large scale for the use of the painter. Of the many methods put in practice, or proposed, for making white lead, the two following are the most important. One of these consists in forming a basic nitrate or acetate of lead by boiling finely powdered litharge with the normal salt. This solution is then brought into contact with carbonic acid gas, whereby all the excess of oxide previously taken up by the normal salt is at once precipitated as white lead, and the solution strained or pressed from the latter is again boiled with litharge and treated with carbonic acid, these processes being susceptible of indefinite repetition, whereby the small loss of normal salt left in the precipitates is compensated. The second, and by far the more ancient method, is rather more complex, and at first sight not very intelligible. A great number of earthen jars are prepared, into each of which is poured a few ounces of crude vinegar; a roll of sheet lead is then introduced in such a manner that it shall neither touch the vinegar nor project above the top of the jar. The vessels are next arranged in a large building, side by side, upon a layer of stable manure, or better, spent tan, and closely covered with boards. A second layer of tan is spread upon the top of the latter, and then a second series of pots; these are in turn covered with boards and decomposing bark, and in this manner a pile of many alternations is constructed. After the lapse of a considerable time, the pile is taken down, and the sheets of lead are removed and carefully unrolled; they are then found to be in great part converted into carbonate, which merely requires washing and grinding to be fit for use. The nature of this curious process is generally explained by supposing that the vapour of vinegar raised by the high temperature due to the fermentation of the dung, or tan, gives rise to the formation of basic acetate of lead, which by contact with the carbon dioxide likewise evolved from the decomposing manure, is converted into basic carbonate.

White lead is a white heavy amorphous powder, appearing under the microscope as an aggregate of round transparent globules, having a diameter of one to four hundred-thousandths of an inch. The product obtained by the method above described is generally preferred to those obtained by other processes, on account of its superior opacity or "body." Commercial white lead, however prepared, always contains a certain proportion of hydroxide.

When clean metallic lead is put into pure water and exposed to the air, a white crystalline scaly powder begins to show itself in a few *hours*, and very rapidly increases in quantity. This substance may

consist of lead hydroxide, formed by the action of the oxygen dissolved in the water upon the lead. It is slightly soluble, and may be readily detected in the water. In most cases, however, the formation of this deposit is due to the action of the carbonic acid dissolved in the water: it consists of carbonate in combination with hydroxide, and is nearly insoluble in water. When common river or spring water is substituted for the pure liquid, this effect is less observable, the little sulphate almost invariably present causing the deposition of a very thin but closely adherent film of lead sulphate upon the surface of the metal, which protects it from further action. It is on this account that leaden cisterns are used with impunity, at least in most cases, for holding water: if the latter were quite pure, it would be speedily contaminated with lead, and the cistern would be soon destroyed. Natural water highly charged with carbonic acid cannot under any circumstances be kept in lead or passed through leaden pipes with safety, the carbonate, though insoluble in pure water, being slightly soluble in water containing carbonic acid.

Lead Sulphide, PbS, occurs native as *Galena* in cubes or other forms of the regular system, having a bluish-grey colour, and a density of 7·25 to 7·7. The same compound is obtained in crystalline form by passing sulphur-vapour over metallic lead, the combination being attended with vivid combustion; also by fusing lead oxide with excess of sulphur; and as a black amorphous precipitate by passing hydrogen sulphide into a solution of nitrate or acetate of lead. A *chlorosulphide*, $PbCl_2,3PS$, is obtained as a yellowish-red precipitate on passing a small quantity of hydrogen sulphide into the solution of a lead salt containing hydrochloric acid. An excess of hydrogen sulphide converts it into the sulphide.

The soluble salts of lead behave with reagents as follows:—

Caustic *potash* and *soda* precipitate a white hydroxide freely soluble in excess. *Ammonia* gives a similar white precipitate not soluble in excess. The *carbonates of potassium*, *sodium*, and *ammonium* precipitate lead carbonate, insoluble in excess. *Sulphuric acid* or a *sulphate* causes a white precipitate of lead sulphate, insoluble in nitric acid. *Hydrogen sulphide* and *ammonium sulphide* throw down black lead sulphide. Lead is readily detected before the blow-pipe by fusing the compound under examination on charcoal with sodium carbonate, when a bead of metal is easily obtained, which may be recognised by its chemical as well as by its physical properties.

An alloy of 2 parts of lead and 1 of tin constitutes *plumbers' solder;* these proportions reversed give a more fusible compound, called *fine solder*. The lead employed in the manufacture of shot is combined with a little arsenic.

THALLIUM.

Symbol, Tl. Atomic weight, 203·6.

This element was discovered by Crookes, in 1861, in the seleniferous deposit of a lead-chamber of a sulphuric acid factory in the Hartz mountains, where iron pyrites is used for the manufacture of sulphuric acid. The name is derived from θαλλός, "green," because the existence of this metal was first recognised by an intense green line, appearing in the spectrum of a flame in which thallium is volatilised. It was at first suspected to be a metalloïd, but further examination proved it to be a true metal. It was first obtained in a distinct metallic form by Crookes towards the end of the year 1861, and soon afterwards by Lamy, who prepared it from the deposit in the lead-chamber of M. Kuhlmann, of Lille, where Belgian pyrites is employed for the manufacture of sulphuric acid.

Thallium appears to be very widely diffused as a constituent of iron and copper pyrites, though it never constitutes more than the 4000th part of the bulk of the ores. It has also been found in lepidolite from Moravia, in mica from Zinnwald in Bohemia, and in the mother-liquors of the salt-works at Nauheim.

Thallium is most economically prepared from the flue-dust of pyrites burners. This substance is stirred up in wooden tubs with boiling water, and the clear liquor, siphoned off from the deposit, is mixed with excess of strong hydrochloric acid, which precipitates impure thallium monochloride. To obtain a pure salt, this crude chloride is added by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred, and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused acid sulphate is now to be dissolved in an excess of water, and an abundant stream of hydrogen sulphide passed through the solution. The precipitate, which may contain arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free hydrogen sulphide is removed. The liquid is now to be rendered alkaline with ammonia, and boiled; the precipitate of iron oxide and alumina, which generally appears in this place, is filtered off; and the clear solution evaporated to a small bulk. Thallium sulphate then separates on cooling, in long clear prismatic crystals.

Metallic thallium may be reduced from the solution of the sulphate either by electrolysis or by the action of zinc.

Thallium is a heavy metal, resembling lead in its physical properties. When freshly cut, it exhibits a brilliant metallic lustre and greyish colour, somewhat between that of silver and that of lead, assuming a slight yellowish tint by friction with harder bodies. It is very soft, being readily cut with a knife, and making a streak *on paper* like plumbago. It is very malleable, is not easily drawn

into wire, but may be readily squeezed into that form by the process technically called "squirting." It has a highly crystalline structure, and crackles like tin when bent. It melts at 294°.

In contact with the air, thallium tarnishes more rapidly than lead, becoming coated with a thin layer of oxide, which preserves the rest of the metal.

The most characteristic property of thallium is the bright green colour which the metal or any of its compounds impart to a colourless flame; and this colour, when viewed by the spectroscope, is seen to be absolutely monochromatic, appearing as one intensely brilliant and sharp green line.

Thallium dissolves in hydrochloric, sulphuric, and nitric acids, the latter attacking it very energetically, with copious evolution of red vapours.

Thallium forms two classes of compounds—namely, the thallious compounds, in which it is univalent: and the thallic compounds, in which it is trivalent. Thus it forms two oxides, Tl_2O and Tl_2O_3, with corresponding chlorides, bromides, iodides, and oxygen-salts. In some of its chemical relations it resembles the alkali-metals, forming a readily soluble and highly alkaline monoxide, a soluble and alkaline carbonate, an insoluble platinochloride, a thallio-aluminic sulphate, similar in form and composition to common potash-alum, and several phosphates exactly analogous in composition to the phosphates of sodium. In most respects, however, it is more nearly allied to the heavy metals, especially to lead, which it resembles closely in appearance, density, melting-point, specific heat, and electric conductivity; also in giving a black precipitate with hydrogen sulphide, and a white precipitate with soluble chlorides.

Thallium Chlorides.—Thallium forms four chlorides, represented by the formulæ TlCl, Tl_4Cl_6, Tl_2Cl_4, and $TlCl_3$; the second and third of which may be regarded as compounds of the monochloride and trichloride.

The *Monochloride* or *Thallious Chloride*, TlCl, is formed by direct combination, the metal burning when heated in chlorine gas; or as a white curdy precipitate resembling silver chloride, by treating the solution of any thallious salt with a soluble chloride. When boiled with water it dissolves like lead chloride, and separates in white crystals on cooling. It forms double salts with trichloride of gold and tetrachloride of platinum. The *platinum salt*, $2TlCl,PtCl_4$, separates as a pale yellow, very slightly soluble, crystalline powder, on adding platinic chloride to thallious chloride.

The *Trichloride* or *Thallic chloride*, $TlCl_3$, is obtained by dissolving the trioxide in hydrochloric acid, or by acting upon thallium, or one of the lower chlorides, with a large excess of chlorine at a gentle heat. It is soluble in water, and separates by evaporation in a vacuum in hydrated crystals; melts easily, and decomposes at a high temperature. It forms crystalline double salts with the chlorides of the alkali-metals.

The *Sesquichloride*, $Tl_4Cl_6 = TlCl_3,3TlCl$, is produced by dissolving thallium or the monochloride in nitromuriatic acid, and separates on cooling in yellow crystalline scales. By aqueous ammonia, potash, or even by thallious oxide, it is instantly decomposed into sesquioxide and monochloride, according to the equation:

$$2Tl_4Cl_6 + 3KHO = Tl_2O_3 + 6TlCl + 3KCl + 3HCl.$$

The *Dichloride*, $Tl_2Cl_4 = TlCl_3,TlCl$, is formed by carefully heating thallium or the monochloride, in a slow current of chlorine. It is a pale yellow substance reduced to sesquichloride by further heating.

The BROMIDES of thallium resemble the chlorides.

Iodides.—*Thallious Iodide*, TlI, is formed by direct combination of its elements, or by double decomposition. It forms a beautiful yellow powder, rather darker than sulphur, and melting, below redness, to a scarlet liquid, which, as the mass cools, remains scarlet for some time after solidification, then changes to bright yellow. The dried precipitate, when spread on paper with a little gum-water, undergoes a similar but opposite change to that experienced by mercuric iodide when heated, the yellow surface when held over a flame suddenly becoming scarlet, and frequently remaining so after cooling for several days; hard friction with a glass rod, however, changes the scarlet colour back to yellow. It is very slightly soluble in water, requiring, according to Crookes, 4453 parts of water at 17·2°, and 842·4 parts at 100°, to dissolve it.

Thallic Iodide, TlI_3, is formed by the action of thallium on iodine dissolved in ether, as a brown solution which gradually deposits rhombic prisms. It forms crystalline compounds with the iodides of the alkali-metals.

Thallium Oxides.—Thallium forms a monoxide and a trioxide.

The *Monoxide* or *Thallious Oxide*, Tl_2O, constitutes the chief part of the crust which forms on the surface of the metal when exposed to the air. It may be prepared by allowing granulated thallium to oxidise in warm moist air, and then boiling with water. The filtered solution first deposits white needles of thallium carbonate, and, on further cooling, yellow needles of the hydroxide, TlHO or Tl_2O,H_2O, which, when left over oil of vitriol in a vacuum, yields the anhydrous monoxide as a reddish-black mass retaining the shape of the crystals. It is partially reduced to metal by hydrogen at a red heat. When fused with sulphur it yields thallious sulphide. It dissolves readily in water, forming a colourless strongly alkaline solution, which reacts with metallic salts very much like caustic potash. This solution treated with zinc, or subjected to electrolysis, yields metallic thallium.

The *Trioxide*, or *Thallic Oxide*, is the chief product obtained by burning thallium in oxygen gas. It is best prepared by adding

potash to the solution of a thallic salt, and drying the precipitate at 260°. It is also formed by electrolysis of thallious sulphate. It is a dark red powder reduced to thallious oxide at a red heat; neutral, insoluble in water and in alkalis. Thallic hydrate, $Tl''HO_2$, is obtained by drying the above-mentioned precipitate at 100°.

Oxygen-salts.—Both the oxides of thallium dissolve readily in acids, forming crystalline salts, soluble in water; there are also a few insoluble thallium salts formed by double decomposition.

Sulphates.—Thallious sulphate, Tl_2SO_4, obtained by evaporating the chloride or nitrate with sulphuric acid, or by heating metallic thallium with that acid, crystallises in anhydrous rhombic prisms, isomorphous with potassium sulphate. It forms, with aluminium sulphate, the salt, $AlTl(SO_4)_2,12H_2O$, isomorphous with common alum; and with the sulphates of magnesium, nickel, &c., double salts containing 6 molecules of water, and isomorphous with magnesium and potassium sulphate, &c. (p. 416).—*Thallic sulphate*, $Tl_2(SO_4)_3,7H_2O$, separates by evaporation from a solution of thallic oxide in dilute sulphuric acid, in thin colourless laminæ, which are decomposed by water, even in the cold, with separation of brown thallic oxide.

Phosphates.—The thallious phosphates form a series nearly as complete as those of the alkali-metals, which they also resemble in their behaviour when heated. There are three *orthophosphates*, containing respectively H_2TlPO_4, HTl_2PO_4, and Tl_3PO_4. The first two are soluble in water; the second is obtained by neutralising dilute phosphoric acid at boiling heat with thallious carbonate, and the first by mixing the dithallious salt with excess of phosphoric acid. The *trithallious salt*, Tl_3PO_4, is very sparingly soluble, and is formed as a crystalline precipitate on mixing the saturated solutions of ordinary disodic phosphate and thallious sulphate; also, together with ammonio-thallious phosphate, by treating the monothallious or dithallious salt with excess of ammonia. There are two *thallious pyrophosphates*, $H_2Tl_2P_2O_7$, and $Tl_4P_2O_7$, both very soluble in water: the first produced by carefully heating monothallious orthophosphate, the second by strongly heating dithallious orthophosphate. Of *thallious metaphosphate*, $TlPO_3$, there are two modifications: the first remaining as a slightly soluble vitreous mass when monothallious orthophosphate is strongly ignited, the second obtained as an easily soluble glass by igniting ammonio-thallious orthophosphate.

Thallic orthophosphate, $Tl''PO_4,2H_2O$, separates as an insoluble gelatinous precipitate on diluting a solution of thallic nitrate mixed with phosphoric acid.

Thallious Carbonate, Tl_2CO_3, is deposited in crystals, apparently trimetric, when a solution of thallious oxide is exposed to the

air. It is soluble in water, and the solution has a slightly caustic taste and alkaline reaction.

Thallium Sulphide, Tl_2S.—This compound is precipitated from all thallious salts by ammonium sulphide, and from the acetate, carbonate, or oxalate, by hydrogen sulphide (incompletely also from the nitrate, sulphate, or chloride), in dense flocks of a greyish or brownish-black colour. Thallic salts appear to be reduced to thallious salts by boiling with ammonium sulphide. Thallium sulphate projected into fused potassium cyanide is reduced to sulphide, which then forms a brittle metal-looking mass, having the lustre of plumbago, and fusing more readily than metallic thallium.

Reactions of Thallium Salts.—The reactions of thallious salts with hydrogen sulphide and ammonium sulphide have just been mentioned.—From their aqueous solutions thallium is rapidly precipitated in metallic crystals by *zinc*, slowly by *iron*. *Soluble chlorides* precipitate difficultly soluble white thallious chloride; soluble *bromides* throw down white, nearly insoluble bromide; soluble *iodides* precipitate insoluble yellow thallious iodide. Caustic *alkalis* and *alkaline carbonates* form no precipitate; *sodium phosphate* forms a white precipitate, insoluble in ammonia, easily soluble in acids.

Potassium chromate gives a yellow precipitate of thallious chromate, insoluble in cold nitric or sulphuric acid, but turning orange-red on boiling in the acid solution.—*Platinic chloride* precipitates a very pale-yellow insoluble double salt.

Thallic salts are easily distinguished from thallious salts by their behaviour with alkalis, and with soluble chlorides or bromides. Their solutions give with *ammonia*, and with *fixed alkalis* and their *carbonates*, a brown gelatinous precipitate of thallic oxide, containing the whole of the thallium. Soluble *chlorides* or *bromides* produce no precipitate in solutions of pure thallic salts; but if a thallious salt is likewise present, a precipitate of sesquichloride or sesquibromide is formed. *Oxalic acid* forms in solutions of thallic salts a white pulverulent precipitate; *phosphoric acid* a white gelatinous precipitate; and *arsenic acid* a yellow gelatinous precipitate. Thallic nitrate gives with *potassium ferrocyanide* a green, and with the *ferricyanide* a yellow precipitate.

In examining a mixed metallic solution, thallium will be found in the precipitate thrown down by ammonium sulphide, together with iron, nickel, manganese, &c. From these metals it may be easily separated by precipitation with potassium iodide or platinic chloride, or by reduction to the metallic state with zinc.

Thallium salts are reduced before the blow-pipe with charcoal and sodium carbonate or potassium cyanide. The green colour imparted to flame by thallium, and the peculiar character of its spectrum, have already been mentioned.

METALS OF THE COPPER GROUP.

Copper—Mercury—Silver.

Each of these metals forms several oxides, and two series of salts, the constitution of which is best represented, as will be presently explained, by regarding the metals as dyads, although two of them, viz., copper and silver, figure in Mendelejeff's series as monads. These metals do not decompose water at a red heat. They are precipitated from their solutions in the metallic state by zinc, iron, and the more oxidable metals, and their lower chlorides, like those of the preceding group, are insoluble in water.

COPPER.

Symbol, Cu (Cuprum). Atomic weight, 63·1.

Copper is a metal of great value in the arts; it sometimes occurs in the metallic state, crystallised in octohedrons, or more frequently in dodecahedrons, but is more abundant in the form of red oxide, and in that of sulphide combined with sulphide of iron, as *yellow copper ore* or *copper pyrites*. Large quantities of the latter substance are annually obtained from the Cornish mines, and taken to South Wales for reduction, which is effected by a somewhat complex process. The principle of this may, however, be easily made intelligible. The ore is roasted in a reverberatory furnace, by which much of the iron sulphide is converted into oxide, while the copper sulphide remains unaltered. The product of this operation is then strongly heated with silicious sand: the latter combines with the iron oxide to a fusible *slag*, and separates from the heavier copper compound. When the iron has, by a repetition of these processes, been got rid of, the copper sulphide begins to decompose in the flame-furnace, losing its sulphur and absorbing oxygen; the temperature is then raised sufficiently to reduce the oxide thus produced, by the aid of carbonaceous matter. The last part of the operation consists in thrusting into the melted metal a pole of birch-wood, the object of which is probably to reduce a little remaining oxide by the combustible gases thus generated. Large quantities of extremely valuable ore, chiefly carbonate and red oxide, have lately been obtained from South Australia and Chili.

Another process, known as the Mansfeld process, and especially adapted for working the cupriferous schists of Mansfeld in Prussia, which are mostly poor in copper, has long been practised in that

sulphides of antimony, arsenic, and bismuth, to form several natural minerals. The several varieties of *fahl-ore*, or *tetrahedrite*, consist of cuprous thioantimonite or thioarsenite, in which the copper is more or less replaced by equivalent quantities of iron, zinc, silver, and mercury. The important ore, called *Copper-pyrites*, is a cuproso-ferric sulphide, $Cu'Fe'''S_2$ or Cu_2S,Fe_2S_3, occurring in tetrahedral crystals of the quadratic system, or in irregular masses. Another species of copper and iron sulphide, containing various proportions of the two metals, occurs native, as *Purple copper* or *Erubescite*, in cubes, octohedrons, and other monometric forms.

Ammoniacal Copper-compounds. — The chlorides, sulphate, nitrate, and other salts of copper, unite with one or more molecules of ammonia, forming, for the most part, crystalline compounds of blue or green colour, some of which may be regarded as salts of metallammoniums (p. 397). Thus cupric chloride forms with ammonia, the compounds, $2NH_3,CuCl_2$, $4NH_3,CuCl_2$, and $6NH_3,CuCl_2$, the first of which may be formulated as *cupro-diammonium chloride*, $(N_2H_6Cu'')Cl_2$. Cupric sulphate forms, in like manner, *cupro-diammonium sulphate*, $(N_2H_6Cu'')SO_4$, which is a deep blue crystalline salt. Cuprous iodide forms with ammonia the compound, $4NH_3,Cu_2I_2$.

Caustic *potash* gives with cupric salts a pale blue precipitate of cupric hydroxide, changing to a blackish-brown anhydrous oxide on boiling.—*Ammonia* also throws down the hydroxide ; but, when in excess, redissolves it, yielding a deep purplish-blue solution.—*Potassium* and *sodium carbonates* give pale blue precipitates of cupric carbonate, insoluble in excess.—*Ammonium carbonate* the same, but soluble with deep blue colour.—*Potassium ferrocyanide* gives a fine red-brown precipitate of cupric ferrocyanide.—*Hydrogen sulphide* and *ammonium sulphide* afford black cupric sulphide, insoluble in ammonium sulphide. Metallic *iron* or *zinc* immersed in a solution of a copper salt quickly becomes coated with metallic copper.

Copper and its compounds impart a green colour to flame. Any compound of copper fused with borax in the oxidising blow-pipe flame forms a transparent glass, which is green while hot, but assumes a fine blue colour on cooling. In the reducing flame the glass becomes opaque, and covered on the surface with liver-coloured streaks of cuprous oxide or metallic copper. This last reaction is facilitated by fusing in the bead a small piece of metallic tin. Copper-compounds, mixed with sodium carbonate or potassium cyanide and heated on charcoal before the blow-pipe, yield metallic copper.

The alloys of copper are of great importance. *Brass* consists of copper alloyed with from 28 to 34 per cent. of zinc; the latter may be added directly to the melted copper, or granulated copper may be heated with calamine and charcoal-powder, as in the old process.

Gun-metal, a most valuable alloy, consists of 90 parts copper and 10 tin. *Bell* and *speculum metal* contain a still larger proportion of tin; these are brittle, especially the last-named. A good bronze for statues is made of 91 parts copper, 2 parts tin, 6 parts zinc, and 1 part lead. The *brass* or *bronze* of the ancients is an alloy of copper with tin, often also containing lead, and sometimes zinc.

SILVER.

Symbol, Ag (Argentum). Atomic weight, 107·66.

SILVER is found in the metallic state, as sulphide, in union with sulphide of antimony and sulphide of arsenic, also as chloride, iodide, and bromide. Among the principal silver mines may be mentioned those of the Hartz mountains in Germany, of Kongsberg in Norway, and, more particularly, of the Andes, in both North and South America.

The greater part of the silver of commerce is extracted from ores so poor as to render any process of *smelting* or fusion inapplicable, even where fuel could be obtained, and this is often difficult to be procured. Recourse, therefore, is had to another method—that of *amalgamation*—founded on the easy solubility of silver and many other metals in metallic mercury.

In Mexico the ore containing small quantities of sulphide and chloride of silver is stamped or ground, together with water, in mills worked by horses or mules; and the fine mud thus produced is mixed on a floor with 3 to 5 per cent. of common salt, which is thoroughly incorporated with the mass by the treading of mules. The mass is then left to itself for a day, after which mercury is added, together with an impure mixture of cupric and ferric salts called "magistral;" then more mercury; and the heap is again trodden by mules till thoroughly incorporated. The amalgamation being completed, the slimy mass is washed in buddles worked by mules, whereby the lighter particles are washed away, and the heavier amalgam is deposited. The amalgam is next filtered through canvas bags and finally distilled, and the silver which is left behind is melted into bars.

The reactions which take place in this amalgamation process are probably as follows. The sulphates of copper and iron (in the magistral) are converted by the chloride of sodium into the corresponding chlorides, which then react with the silver sulphide, forming silver chloride:

$$2CuCl_2 + Ag_2S = Cu_2Cl_2 + 2AgCl + S,$$

the cuprous chloride thus produced acting further on the silver sulphide and forming more silver chloride:

$$Cu_2Cl_2 + Ag_2S = Cu_2S + 2AgCl.$$

The resulting silver chloride is held in solution by the sodium chloride, and on addition of metallic mercury, is decomposed, yielding calomel and metallic silver. All the mercury thus converted into calomel—amounting to about twice the weight of the silver obtained—is lost.

In Nevada, where the ores are of various degrees of richness, the richer ones are usually roasted with common salt, whereby the silver sulphide is converted into chloride; the roasted and pulverised mass is then introduced, together with water, scrap-iron, and mercury, into barrels rotating on a horizontal axis; and the metallic silver thereby set free is dissolved out by mercury. This barrel-process was first worked at Schemnitz in Hungary, and afterwards at Freiberg and Mansfeld, but is now no longer practised in Europe.

Considerable loss often occurs in the amalgamation process from the combination of a portion of the mercury with sulphur, oxygen, &c., whereby it is brought into a pulverulent condition, known as "flouring," and is then liable to be washed away, together with the silver it has taken up. This inconvenience may be prevented, as suggested by Mr. Crookes, by amalgamating the mercury with 1 or 2 per cent. of sodium, which, by its superior affinity for sulphur and oxygen, prevents the mercury from becoming floured.

A considerable quantity of silver is obtained from argentiferous galena; in fact, almost every specimen of native lead sulphide is found to contain traces of this metal. When the proportion rises to a certain amount, it becomes worth extracting. The ore is reduced in the usual manner, the whole of the silver remaining with the lead; the latter is then re-melted in a large vessel, and allowed to cool slowly until solidification commences. The portion which first crystallises is nearly pure lead, the alloy with silver being *more fusible than lead itself:* this is drained away by means of a perforated ladle, and is found to contain nearly the whole of the silver [Pattinson's process]. This rich mass is next exposed to a red heat on the shallow hearth of a furnace, while a stream of air is allowed to impinge upon its surface; oxidation then takes place with great rapidity, the fused oxide or litharge being constantly swept from the metal by the blast. When the greater part of the lead has been thus removed, the residue is transferred to a cupel or shallow dish made of bone-ashes, and again heated: the last portion of the lead is now oxidised, and the oxide sinks in a melted state into the porous vessel, while the silver, almost chemically pure, and exhibiting a brilliant surface, remains behind.

Extraction of Silver in the Wet Way.—Silver may be extracted from argentiferous copper pyrites: (1.) By roasting the ore, whereby the sulphides of copper and iron are converted into insoluble oxides, while the silver is obtained as soluble sulphate, from the solution of which, obtained by lixiviating the roasted ore with hot water, the silver is easily precipitated in the metallic state. (2.) By roasting the ore with sodium chloride, to convert the silver into chloride, dissolving out this compound with sodium thiosulphate; precipitating

the silver from the resulting solution as sulphide by means of sodium sulphide; and strongly heating the precipitated sulphide in a muffle furnace, whereby the sulphur is burnt away, and the silver is left. (3.) By Claudet's process, which is applied to the extraction of the small quantity of silver contained in the burnt pyrites of the sulphuric acid works (pp. 194, 387). The cupreous tank-liquors obtained in this process contain the silver as chloride, held in solution by sodium chloride; and from this solution the silver may be thrown down, in the form of iodide, by adding a solution of kelp; a very small quantity of gold is precipitated at the same time.

Purification.—Pure silver is easily obtained. The impure metal is dissolved in nitric acid: if it contains copper, the solution will have a blue tint; gold will remain undissolved as a black powder. The solution is mixed with hydrochloric acid or with common salt, and the white, insoluble, curdy precipitate of silver chloride is washed and dried. This is then mixed with about twice its weight of anhydrous sodium carbonate, and the mixture, placed in an earthen crucible, is gradually raised to a temperature approaching whiteness, during which the sodium carbonate and the silver chloride react upon each other; carbon dioxide and oxygen escape, while metallic silver and silver chloride result: the former melts into a button at the bottom of the crucible, and is easily detached. The following is perhaps the most simple method for the reduction of silver chloride. The silver-salt is covered with water, to which a few drops of sulphuric acid are added; a plate of zinc is then introduced; the silver chloride soon begins to decompose, and after a short time is entirely converted into metallic silver. The silver thus obtained is grey and spongy; it is ultimately purified by washing with slightly acidulated water.

Properties.—Pure silver has a perfect white colour and a strong lustre: it is exceedingly malleable and ductile, and is probably the best conductor both of heat and electricity known. Its specific gravity is 10·5. In hardness it lies between gold and copper. It melts at a bright red heat. Silver is unalterable by air and moisture: it refuses to oxidise at any temperature, but possesses the remarkable faculty already noticed of absorbing many times its volume of oxygen when strongly heated in an atmosphere of that gas, or in common air. The oxygen is again disengaged at the moment of solidification, and gives rise to the peculiar arborescent appearance often remarked on the surface of masses or buttons of pure silver. The addition of 2 per cent. of copper is sufficient to prevent the absorption of oxygen. Silver oxidises when heated with fusible siliceous matter, as glass, which it stains yellow or orange, from the formation of a silicate. It is but slightly attacked by hydrochloric acid; boiling oil of vitriol converts it into sulphate, with evolution of sulphurous oxide; nitric acid, even dilute and in the cold, dissolves it readily. The tarnishing of surfaces of silver exposed to the air is due to hydrogen sulphide, the metal having a strong attraction for sulphur.

Silver Dioxide, $Ag_2O_2 = \begin{matrix} Ag—O \\ | \quad | \\ Ag—O \end{matrix}$, is a black crystalline substance which forms upon the positive electrode of a voltaic arrangement employed to decompose a solution of silver nitrate. It is reduced by heat; evolves chlorine when acted upon by hydrochloric acid; explodes when mixed with phosphorus and struck; and decomposes solution of ammonia, with great energy and rapid disengagement of nitrogen gas.

Oxysalts of Silver.—*Silver Sulphate*, Ag_2SO_4, may be prepared by boiling together oil of vitriol and metallic silver, or by precipitating a concentrated solution of silver nitrate with an alkaline sulphate. It dissolves in 88 parts of boiling water, and separates in great measure in the crystalline form on cooling, being but slightly soluble at a low temperature. It forms with ammonia a crystallisable compound which is freely soluble in water, contains $2NH_3,Ag_2SO_4$, and may therefore be regarded as *argentammonium sulphate*, $(NH_3Ag)_2SO_4$.

Silver Dithionate, $Ag_2S_2O_6$, is a soluble crystallisable salt, permanent in the air. The *thiosulphate*, $Ag_2S_2O_3$, is insoluble, white, and very prone to decomposition: it combines with the alkaline thiosulphates, forming soluble compounds distinguished by an intensely sweet taste. The alkaline thiosulphates dissolve both oxide and chloride of silver, and give rise to similar salts, an oxide or chloride of the alkali-metal being at the same time formed: hence the use of alkaline thiosulphates in fixing photographic pictures (p. 99).

Silver Nitrate, $AgNO_3$, is prepared by dissolving silver in nitric acid, and evaporating the solution to dryness, or until it is strong enough to crystallise on cooling. The crystals are colourless, transparent, anhydrous tables, soluble in an equal weight of cold and in half that quantity of boiling water; they also dissolve in alcohol. They fuse when heated, like those of nitre, and at a high temperature suffer decomposition: the *lunar caustic* of the surgeon is silver nitrate which has been melted and poured into a cylindrical mould. The salt blackens when exposed to light, more particularly if organic matters of any kind are present, and is frequently employed to communicate a dark stain to the hair; it enters into the composition of the "indelible" ink used for marking linen. The black stain has been thought to be metallic silver; it may possibly be argentous oxide. Pure silver nitrate may be prepared from the metal alloyed with copper: the alloy is dissolved in nitric acid, the solution evaporated to dryness, and the mixed nitrates cautiously heated to fusion. A small portion of the melted mass is removed from time to time for examination: it is dissolved in water, filtered, and ammonia added to it in excess. While any copper-salt remains undecomposed, the liquid will be blue, but when that no longer happens, the nitrate may be left to cool, dissolved in water, and filtered from the black oxide of copper.

Silver Carbonate is a white insoluble substance obtained by mixing solutions of silver nitrate and sodium carbonate. It is blackened and decomposed by boiling.

Silver Sulphide, Ag_2S, is a soft, grey, and somewhat malleable substance, found native in the crystallised state, and easily produced by melting together its constituents, or by precipitating a solution of silver with hydrogen sulphide. It is a strong sulphur-base, and combines with the sulphides of antimony and arsenic: examples of such compounds are found in the beautiful minerals, *dark* and *light-red silver ore.*

Ammonia-compound of Silver; *Berthollet's Fulminating Silver.* —This is a black, explosive compound formed by digesting precipitated argentic oxide in ammonia. While moist, it explodes only when rubbed with a hard body, but when it is dry, the touch of a feather is sufficient. The ammonia retains some of this substance in solution, and deposits it in small crystals by spontaneous evaporation. A similar compound exists containing oxide of gold.

Argentic chloride slowly absorbs ammonia-gas, forming the compound $3NH_3,Ag_2Cl_2$, which readily gives off its ammonia when heated, and may be used for the preparation of pure ammonia gas—or of liquid ammonia if heated in a sealed tube. Argentic iodide likewise absorbs ammonia-gas, forming the compound NH_3,Ag_2I_2, which gives off its ammonia on exposure to the air.

Soluble silver salts are perfectly characterised by the white curdy precipitate of silver chloride, darkening on exposure to light, and insoluble in hot nitric acid, which is produced by the addition of any soluble *chloride.* Lead and mercury are the only metals which can be confounded with silver in this respect; but lead chloride is soluble to a great extent in boiling water, and is deposited in brilliant acicular crystals when the solution cools; and mercurous chloride is instantly blackened by ammonia, whereas silver chloride is dissolved thereby.

Solutions of silver are reduced to the metallic state by *iron, copper, mercury,* and other metals. They give with *hydrogen sulphide* a black precipitate of argentic sulphide, insoluble in ammonium sulphide; with *caustic alkalis,* a brown precipitate of argentic oxide; and with *alkaline carbonates,* a white precipitate of argentic carbonate, both precipitates being easily soluble in ammonia. Ordinary *sodium phosphate* forms a yellow precipitate of argentic orthophosphate; *potassium chromate* or *bichromate,* a red brown precipitate of argentic chromate.

The economical uses of silver are many; it is admirably adapted for culinary and other similar purposes, not being attacked in the slightest degree by any of the substances used for food. It is neces-

$3HgO,SO_3$. Long-continued washing with hot water entirely removes the remaining acid, and leaves pure mercuric oxide.

Mercurous Sulphate, Hg_2SO_4, falls as a white crystalline powder when sulphuric acid is added to a solution of mercurous nitrate: it is but slightly soluble in water.

Mercury Sulphides.—*Mercuric Sulphide*, HgS, occurs native as cinnabar, a dull red mineral, which is the most important ore of mercury. Hydrogen sulphide passed in small quantity into a solution of mercuric nitrate, or chloride, forms a white precipitate, which is a compound of mercuric sulphide with the salt itself. An excess of the gas converts the whole into sulphide, the colour at the same time changing to black. When this black sulphide is sublimed, it becomes dark red and crystalline, but undergoes no change of composition: it is then *cinnabar* or *vermilion*. Mercuric sulphide is most easily prepared by subliming an intimate mixture of 6 parts of mercury and 1 part of sulphur, and reducing the resulting cinnabar to very fine powder, the beauty of the tint depending much upon the extent to which division is carried. The red or crystalline sulphide may also be formed directly, without sublimation, by heating the black precipitated substance in a solution of potassium pentasulphide. Mercuric sulphide is soluble to a certain extent in the alkaline sulphides, and forms with them crystallisable compounds.

When vermilion is heated in the air, it yields metallic mercury and sulphurous oxide: it resists the action both of caustic alkalis in solution, and of strong mineral acids, even nitric, and is attacked only by nitro-muriatic acid.

Mercurous sulphide, Hg_2S, is obtained by passing hydrogen sulphide into a solution of mercurous nitrate, as a black precipitate, which is resolved at a gentle heat into mercuric sulphide and metallic mercury.

Ammoniacal Mercury Compounds.—Mercurammonium Salts.—By the action of ammonia and its salts on mercury compounds, a variety of substances are formed, which may be regarded as salts of mercurammoniums—that is, of ammonium-molecules in which the hydrogen is more or less replaced by mercury, in the proportion of 100 or 200 parts of mercury to 1 part of hydrogen, according as the compound is formed from a mercurous or a mercuric salt. The following are the most important of these compounds:—

Mercuric Compounds. — *Mercuro-diammonium chloride*, $(N_2H_6Hg'')Cl_2$, known in pharmacy as *fusible white precipitate*, is produced by adding potash to a solution of ammonio-mercuric chloride, $(2NH_4Cl,HgCl_2)$, or by dropping solution of mercuric chloride into a boiling solution of sal-ammoniac containing free ammonia, as long as the resulting precipitate redissolves: it then separates on cooling in regular dodecahedrons. At a gentle heat it

gives off ammonia, leaving a chloride of mercurammonium and hydrogen, $(NH_2Hg'')Cl,HCl$:

$$N_2H_6Hg''Cl_2 = NH_3Hg''Cl_2 + NH_3.$$

Mercurammonium chloride, $(NH_2Hg'')Cl$.—This salt, known in pharmacy as *infusible white precipitate*, is formed by adding ammonia to a solution of mercuric chloride. When first produced, it is bulky and white, but by contact with hot water, or by much washing with cold water, it is converted into hydrated dimercurammonium chloride, NHg''_2Cl,H_2O.

Trimercuro-diammonium nitrate, $(N_2H_2Hg''_3)(NO_3)_2,2H_2O$, is formed as a white precipitate, on mixing a dilute and very acid solution of mercuric nitrate with very dilute ammonia.

Trimercuro-diamine, $N_2Hg''_3$, a compound derived from a double molecule of ammonia, N_2H_6, by substitution of 3 atoms of bivalent mercury for 6 atoms of hydrogen, is formed by passing dry ammonia gas over dry precipitated mercuric oxide:

$$3HgO + 2NH_3 = N_2Hg_3 + 3H_2O.$$

The excess of oxide being removed by nitric acid, the trimercuro-diamine is obtained as a dark-brown powder, which explodes by heat, friction, percussion, or contact with oil of vitriol, almost as violently as nitrogen chloride.

Dimercurammonium chloride, NHg''_2Cl,H_2O, is obtained, as already observed, by boiling mercurodiammonium chloride (infusible white precipitate) with water. It is a heavy, granular, yellow powder, which turns white again when treated with sal-ammoniac.

Dimercurammonium iodide, NHg''_2I,H_2O.—This compound may be formed by digesting the corresponding chloride in a solution of potassium iodide; or by heating mercuric iodide with excess of aqueous ammonia:

$$2HgI_2 + 4NH_3 + H_2O = NHg''_2I,H_2O + 3NH_4I;$$

also by passing ammonia gas over mercuric oxy-iodide:

$$Hg_4I_2O_3 + 2NH_3 = 2(NHg''_2I,H_2O) + H_2O;$$

and, lastly, by adding ammonia to a solution of potassio-mercuric iodide mixed with caustic potash:

$$2(2KI,HgI_2) + NH_3 + 3KHO = NHg''_2I,H_2O + 7KI + 2H_2O.$$

This last reaction affords an extremely delicate test for ammonia. A solution of potassio-mercuric iodide is prepared by adding potassium iodide to a solution of corrosive sublimate, till a portion only of the resulting red precipitate is redissolved, then filtering, and mixing the filtrate with caustic potash. The liquid thus obtained forms, with a very small quantity of ammonia, either free or in the

METALS OF THE YTTRIUM GROUP.

This group includes a considerable number of metals occurring in gadolinite, cerite, samarskite, and other rare minerals. The extraction and separation of the oxides of these metals is complex and difficult, and the number of distinct oxides or earths thus obtainable is not exactly known, the discovery of some of them, announced by certain chemists, having been denied by others; but the existence of the nine following may perhaps be considered as established :—

	Symbol.	At. w.		Symbol.	At. w.
Scandium . .	Sc	44	Samarium. .	Sm	150
Yttrium . .	Y	89	Terbium . .	Tb	149
Lanthanum .	La	138	Decipium . .	Dp	159
Cerium . .	Ce	141·6	Erbium . .	Er	169
Didymium . .	Di	145·4	Ytterbium .	Yb	173

Yttrium, Erbium, Terbium, Ytterbium, Scandium, Decipium.

These metals exist as silicates in the gadolinite or ytterbite of Ytterby in Sweden, and in a few other rare minerals; also as niobates and tantalates in the samarskite of North Carolina.

To obtain the earths yttria and erbia (including terbia and ytterbia), gadolinite is digested with hydrochloric acid, and the solution separated from the silica is treated with oxalic acid, which throws down the oxalates of erbium and yttrium, together with those of calcium, cerium, lanthanum, and didymium. These oxalates are converted into nitrates; the solution is treated with excess of solid potassium sulphate, to separate the cerium metals; the erbia and yttria, which still remain in solution, are again precipitated by oxalic acid; and the same treatment is repeated, till the solution of the mixed earths, when examined by the spectroscope, no longer exhibits the absorption-bands characteristic of didymium. To separate the erbia and yttria, they are again precipitated by oxalic acid. The oxalates are converted into nitrates, and the nitrates of erbium and yttrium are separated by a series of fractional crystallisations, the erbium salt being the less soluble of the two, and crystallising out first.

This process, for the details of which we must refer to larger works,* effects the separation of yttria from erbia, terbia, and ytterbia; but no method of completely separating the last three earths one from the other has yet been devised. The proportions of these earths in gadolinite are however variable, some specimens containing nearly pure erbia, whilst others are nearly free from that earth. Ytterbia has been obtained in very small quantity only.

* Roscoe and Schorlemmer's Treatise on Chemistry, vol. ii. pt. i. p. 420; and Watts's Dictionary of Chemistry, vol. v. p. 721.

Erbia, Eb_2O_3, obtained by ignition of erbium nitrate or oxalate, has a faint rose colour. It does not melt at the strongest white heat, but aggregates to a spongy mass, glowing with an intense green light, which, when examined by the spectroscope, exhibits a *continuous* spectrum intersected by a number of bright bands. Solutions of erbium salts, on the other hand, give an absorption-spectrum exhibiting dark bands, and *the points of maximum intensity of the light bands in the emission-spectrum of glowing erbia coincide exactly in position with the points of greatest darkness in the absorption-spectrum.* The position of these bands is totally different from those in the emission and absorption-spectra of didymium.

Erbium salts have a rose-red colour, deeper in the hydrated than in the anhydrous state; they have an acid reaction and sweet astringent taste. The *sulphate*, $EbSO_4,8H_2O$, forms light rose-coloured crystals, isomorphous with the sulphates of yttrium and didymium.

Yttria, Y_2O_3, is a soft, nearly white powder, which when ignited glows with a pure white light, and yields a spectrum not containing any bright bands, like that of erbia. It does not unite directly with water, but is precipitated as a hydroxide by alkalis from solutions of yttrium salts. It dissolves slowly but completely in hydrochloric, nitric, and sulphuric acids, forming colourless solutions which do not exhibit any absorption-spectrum. *Yttrium sulphate*, $Y_2(SO_4)_3,8H_2O$, forms small colourless crystals.

Metallic erbium has not yet been isolated. Yttrium (containing erbium) was obtained by Berzelius, as a blackish-grey powder by igniting yttrium chloride with potassium.

Terbia, Tb_2O_3, is most advantageously prepared from the samarskite of North Carolina, in which it exists as niobate, mixed with only small quantities of erbia and yttria. The mixture of oxides obtained from this mineral is dissolved in nitric acid; the solution is treated with potassium sulphate to precipitate the cerium metals; and the solution of the remaining nitrates is mixed with a saturated solution of sodium sulphate, whereby a crystalline sulphate is obtained, which, when treated with ammonium oxalate, yields an insoluble oxalate, leaving on ignition a dark yellow oxide. This oxide is dissolved in a large excess of strong nitric acid; a hot concentrated solution of oxalic acid is dropped in till a permanent precipitate is formed; the liquid, after 24 hours, is decanted, and again fractionally precipitated with oxalic acid; and this treatment is repeated three times more. The united precipitates are then calcined and redissolved in nitric acid; the resulting solution is likewise subjected to a series of fractional precipitations with oxalic acid, and the precipitated oxalates are calcined. When the earths thus purified are dissolved by small quantities in dilute formic acid, and the clear solution is heated and slightly concentrated, a white precipitate is obtained, yielding on ignition a

Two other aluminium sulphates, with excess of base, are also described, one of which is insoluble in water.

Aluminium sulphate combines with the sulphates of potassium, sodium, and ammonium, and the other alkali-metals, forming double salts of great interest, the *alums*. Common alum, the source of all the preparations of alumina, contains $AlK(SO_4)_2,12H_2O$. It is manufactured on a very large scale from a kind of slaty clay loaded with iron bisulphide, which abounds in certain localities. This is gently roasted, and then exposed to the air in a moistened state; oxygen is absorbed; the sulphur becomes acidified; ferrous sulphate and aluminium sulphate are produced, and afterwards separated by lixiviation with water. The solution is next concentrated, and mixed with a quantity of potassium chloride, which decomposes the iron-salt, forming ferrous chloride and potassium sulphate, and the latter combines with the aluminium sulphate to form alum. By crystallisation the alum is separated from the highly soluble iron chloride, and afterwards easily purified by a repetition of the process.

Potassium-alum crystallises in colourless transparent octohedrons, which often exhibit the faces of the cube. It has a sweetish and astringent taste, reddens litmus-paper, and dissolves in 18 parts of water at 15·5°, and in its own weight of boiling water. Exposed to heat, it is easily rendered anhydrous, and by a very high temperature it is decomposed. The crystals have little tendency to change in the air. Alum is largely used in the arts, in preparing skins, dyeing, &c.: it is occasionally contaminated with iron oxide, which interferes with some of its applications. The celebrated Roman alum, made from *alum-stone*, a felspathic rock altered by sulphurous vapours, was once much prized on account of its freedom from this impurity. A mixture of dried alum and sugar, carbonised in an open pan, and then heated to redness in a glass flask, contact with air being avoided, furnishes *Homberg's pyrophorus*, which ignites spontaneously on exposure to the air. The essential ingredient is, in all probability, finely divided potassium sulphide.

A process has been patented by Messrs. Duncan and Newlands for separating the potash from syrups of beet and cane sugar by means of aluminium sulphate, the potash being thereby precipitated in the form of alum. A solution of aluminium sulphate of a density corresponding with about 27° of Baumé's hydrometer is added to the cold syrup having a density of about 36° B., in quantity sufficient to precipitate the whole of the potash present; the mixture is well stirred for fifteen minutes to an hour; and the whole left at rest for four or five hours till the deposit has completely subsided. This deposit consists of small crystals, technically known as "alum meal." Considerable quantities of alum are now made by this process.

Sodium-alum, in which sulphate of sodium replaces sulphate of potassium, has a form and constitution similar to that of common alum: it is, however, much more soluble and difficult to crystallise.

Ammonium-alum, containing NH_4 instead of K, very closely resembles common potassium-alum, having the same figure, appearance, and constitution, and nearly the same degree of solubility as that substance. As the value of potassium salts is continually increasing, ammonium-alum, which may be used in dyeing with the same advantage as the corresponding potassium salt, has almost entirely replaced the potassium-alum in that process. When heated to redness, ammonium-alum yields pure alumina.

Cæsium-alum, $AlCs(SO_4)_2,12H_2O$, and *Rubidium-alum*,

$$AlRb(SO_4)_2,12H_2O,$$

resemble potassium-alum. A *silver-alum*, $AlAg(SO_4)_2,12H_2O$, is formed by heating equivalent quantities of argentic and aluminium sulphates till the former is dissolved. It crystallises in regular octohedrons, and is resolved by water into its component salts. There is also a *thallium-alum*, $AlTl(SO_4)_2,12H_2O$, which crystallises in regular octohedrons.

Lastly, there are alums isomorphous with those just described, in which the aluminium is replaced by iron, chromium, and manganese: for example, *potassio-ferric sulphate* or *potassium-iron alum*, $FeK(SO_4)_2,12H_2O$; *ammonio-chromic sulphate*, $Cr(NH_4)(SO_4)_2,12H_2O$. These will be described further on.

Phosphates.—The *normal salt*, $AlPO_4$ or $Al_2(PO_4)_2$, is obtained on adding a neutral solution of alum to a solution of ordinary sodium phosphate, as a gelatinous precipitate, which dissolves in caustic potash or soda and in mineral acids, but not in ammonia or in acetic acid. On adding ammonia to a solution of this salt in hydrochloric acid, a precipitate is formed, consisting of a basic salt, $3Al_2(PO_4)_2,Al_2(OH)_6 + 15H_2O$. The mineral *wavellite*, which occurs in trimetric crystals, or in hemispherical or globular concretions having a radiate structure, is likewise a basic aluminium phosphate having the composition $2Al_2(PO_4)_2$, $Al_2(OH)_6 + 9H_2O$: it also contains small quantities of fluorine and sometimes of chlorine. *Turquois* is another basic aluminium phosphate, containing $Al_2(PO_4)_2,Al_2(OH)_6 + 2H_2O$.

Silicates.—Silicates of aluminium enter into the composition of a number of crystallised minerals, among which felspar, by reason of its abundant occurrence, occupies a prominent place. Granite, porphyry, trachyte, and other ancient unstratified rocks, consist in great part of this mineral, which, under particular circumstances, by no means well understood, and particularly by the action of the carbonic acid of the air, suffers complete decomposition, being converted into a soft friable mass of earthy matter. This is the origin of clay: the change itself is seen in great perfection in certain districts of Devonshire and Cornwall, the felspar of the fine white granite of those localities being often disintegrated to a great depth, and the rock altered to a substance resembling soft mortar. By

enamel, has yet to be executed; after which the pieces are again heated, in order to flux the colours. The operation has sometimes to be repeated more than once.

The manufacture of porcelain in Europe is of modern origin: the Chinese have possessed the art from the commencement of the seventh century, and their ware is, in some respects, altogether unequalled. The materials employed by them are known to be *kaolin* or decomposed felspar; *petuntze*, or quartz reduced to fine powder; and the ashes of fern, which contain potassium carbonate.

Stoneware.—This is a coarse kind of porcelain, made from clay containing oxide of iron and a little lime, to which it owes its partial fusibility. The glazing is performed by throwing common salt into the heated furnace; this is volatilised, and decomposed by the joint agency of the silica of the ware and of the vapour of water always present; hydrochloric acid and soda are produced, the latter forming a silicate, which fuses over the surface of the ware, and gives a thin, but excellent glaze.

Earthenware.—The finest kind of earthenware is made from a white secondary clay, mixed with a considerable quantity of silica. The articles are thoroughly dried and fired; after which they are dipped into a readily fusible glaze mixture, of which lead oxide is usually an important ingredient, and, when dry, reheated to the melting point of the latter. The whole process is much easier of execution than the making of porcelain, and demands less care. The ornamental designs in blue and other colours, so common upon plates and household articles, are printed upon paper in enamel pigment mixed with oil, and transferred, while still wet, to the unglazed ware. When the ink becomes dry, the paper is washed off, and the glazing completed.

The coarser kinds of earthenware are sometimes covered with a whitish opaque glaze, which contains the oxides of lead and tin; such glaze is very liable to be attacked by acids, and is dangerous for culinary vessels.

Crucibles, when of good quality, are very valuable to the chemist. They are made of clay free from lime, mixed with sand or ground ware of the same description. The Hessian and Cornish crucibles are among the best. Sometimes a mixture of plumbago and clay is employed for the same purpose; and powdered coke has been also used with the earth: such crucibles bear rapid changes of temperature with impunity.

INDIUM.

Symbol, In. Atomic weight, 114·4.

This metal was discovered in 1863 by Reich and Richter, in the zinc-blende of Freiberg, and has since been found in a few other zinc-ores and in the flue-dust of zinc furnaces. The metallic sponge which remains when the crude zinc of the Freiberg works is dissolved in dilute sulphuric acid, contains the whole of the indium (0·045 per cent.), together with lead, arsenic, cadmium, and iron. It is dissolved in nitric acid; the lead, arsenic, and cadmium are precipitated by hydrogen sulphide; and the filtered solution is heated with potassium chlorate to bring all the iron to the state of ferric salt, and then treated with ammonia, which precipitates the indium as a hydroxide, together with iron and zinc. The precipitate is dissolved in acetic acid; and the indium, precipitated as sulphide by hydrogen sulphide, is freed from traces of iron and zinc by dissolving the precipitate in dilute hydrochloric acid, precipitating the indium by agitation with barium carbonate, dissolving out the indium hydroxide by dilute sulphuric acid, and reprecipitating with ammonia.

Indium, reduced from its oxide by ignition with sodium, is a silver-white metal, soft and ductile, has a specific gravity of 7·421, melts at 176°, and is less volatile than cadmium or zinc. When heated to redness in the air, it burns with a violet flame, and is converted into the yellow sesquioxide. Heated in chlorine, it burns with a yellow-green light, and forms a chloride, which sublimes without fusion at an incipient red heat, in soft white laminæ.

Indium dissolves in the strong mineral acids, and is precipitated from the solutions by *zinc* and *cadmium*. *Hydrogen sulphide* precipitates it completely, as a yellow sulphide, from a solution of its acetate, and from neutral solutions of indium salts in general, but not from solutions containing excess of the strong mineral acids. *Ammonia* and *sodium carbonate* produce white precipitates insoluble in excess: *caustic potash* or *soda* throws down white indium hydroxide soluble in excess of the alkali. *Ammonium carbonate* forms a white precipitate soluble in excess, and reprecipitated on boiling. *Barium carbonate* precipitates indium completely.

The spectrum of indium is characterised by two indigo-coloured lines, one very bright and more refrangible than the blue line of strontium, the other fainter and still more refrangible, and approaching the blue line of potassium. It was the observation of this peculiar spectrum that led to the discovery of the metal.

The formulæ of the principal normal indium compounds are as follows:—

Chloride	$InCl_3$
Indium and Ammonium chloride,	$2NH_4Cl,InCl_3 + H_2O$
Yellow oxide	In_2O_3
Hydroxide	InH_3O_3
Nitrate	$In(NO_3)_3$
Sulphate	$In_2(SO_4)_3 + 9H_2O$.

The yellow oxide, heated in a stream of hydrogen, is successively reduced to a green, a grey, and a black oxide, and at a low red heat to the metallic state.

GALLIUM.

Symbol, Ga. Atomic weight, 69·8.

This metal was discovered in 1875 by Lecoq de Boisbaudran,* in a zinc-blende from the mine of Pierrefitte, in the valley of Argeles, Pyrenees, and has likewise been found, though always in very small quantity, in blendes from other localities. It is separated by dissolving the blende in nitromuriatic acid, immersing plates of zinc in the solution till the disengagement of hydrogen becomes slow,—whereby copper, lead, cadmium, and other metals are precipitated,—and then boiling the clear liquid for several hours with a large excess of zinc, which throws down alumina, basic zinc-salts, and oxide of gallium. This precipitate is redissolved in hydrochloric acid; the solution again boiled with zinc; the resulting precipitate, which contains the gallium in a more concentrated form, is redissolved in hydrochloric acid; the solution mixed with ammonium acetate is treated with hydrogen sulphide, which throws down the zinc and gallium as sulphides, leaving the aluminium in solution; and this treatment is repeated to ensure the complete separation of the alumina. The white sulphides of zinc and gallium are then dissolved in hydrochloric acid; the solution is fractionally precipitated with sodium carbonate, the gallium going down chiefly in the first portions; and, to complete the separation of the zinc, the gallium oxide is dissolved in sulphuric acid and reprecipitated by excess of ammonia; this dissolves all the zinc oxide, and the greater part of the gallium oxide, which may be reprecipitated by boiling the liquid to expel the free ammonia.

Metallic gallium is obtained by electrolysing a solution of the oxide in potash or ammonia with platinum electrodes, the gallium being deposited on the negative plate as a compact, closely adhering crust, which may be detached by bending the plate backwards and forwards under cold water.

Gallium is a hard metal somewhat whiter than platinum, and acquires a good polish by pressure; it is sectile and somewhat

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* Comptes rendus, lxxxi. 493.

malleable; its specific gravity is 5·9, which is intermediate between that of aluminum (2·7) and that of indium (7·4). Its melting point is 30·1°, so that it liquefies when pressed between the fingers; frequently also it remains liquid for a long time even when cooled nearly to 0°. The melted metal adheres to glass, forming a mirror whiter than that produced by mercury. When heated to bright redness in contact with the air, it oxidises merely on the surface, and does not volatilise.

Gallium forms a very bright electric spectrum, exhibiting a brilliant line and a fainter band in the violet. In a gas-flame only the line is exhibited, and even this is very faint and fugitive. It was by these spectroscopic characters that the existence of gallium was first recognised.

Gallium chloride is very soluble and deliquescent. Its aqueous solution is clear when highly concentrated, but becomes turbid on addition of water; the precipitate (probably an oxychloride) dissolves but very slowly in hydrochloric acid. A slightly acidulated solution of the chloride evaporated at a gentle heat, deposits needles which act strongly on polarised light. The *sulphate* is not deliquescent.

Gallium forms an *ammonia-alum*, which crystallises in octohedrons like common alum; it dissolves in cold water, but the solution becomes turbid on boiling, and is decomposed by heating with acetic acid. The existence of this alum shows that the oxide of gallium is represented by the formula Ga_2O_3, and its chloride by $GaCl_3$, or Ga_2Cl_6.

Solutions of gallium salts give with *ammonium sulphide* a white precipitate of gallium sulphide insoluble in excess of the reagent. The same precipitate is formed by *hydrogen sulphide* in presence of acetic, but not of hydrochloric acid. *Ammonia* and *carbonate of ammonia* give white precipitates soluble in excess. Slightly acid solutions of the chloride and sulphate are not precipitated in the cold by *ammonium acetate;* but the neutral solutions are clouded thereby. Gallium oxide is easily precipitated by *barium carbonate*, *cupric hydroxide*, and *potassium ferrocyanide*, the last-mentioned reagent affording an extremely delicate test of its presence.*

In a mixed solution of gallium and aluminium, the latter is precipitated before the gallium, and in a mixed solution of gallium and indium, the gallium goes down first; in point of basicity, therefore, gallium is intermediate between aluminium and indium.

The existence of a metal having the atomic weight and properties of gallium was predicted, as already observed, by Mendelejeff (p. 294).

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* On the separation of gallium from other metals, see Lecoq de Boisbaudran: Comptes rendus, xciv. 1154, 1439, 1625; xcv. 157, 410, 503, 703, 1192, 1332; xcvi, 152; and Journal of the Chemical Society, xlii. 897, 1323; xliv. 21, 153, 156, 293, and 715.

METALS OF THE IRON GROUP.

Manganese.	Cobalt.
Iron.	Nickel.

These metals form basic oxides, MO, in which they are bivalent, and corresponding sulphates, which unite with the sulphates of the alkali-metals, forming double sulphates isomorphous with those of the magnesium group (p. 416), *e.g.*, $K_2Fe(SO_4)_2 + 6H_2O$. Manganese and iron also form sesquioxides, which, like alumina, act as weak bases, and their sulphates, like aluminium sulphate, unite with sulphates of alkali-metal, forming alums isomorphous with common alum ; *e.g.*, *potassio-ferric sulphate*, $KFe'''(SO_4)_2 + 12H_2O$ or $K_2(Fe_2)^{vi}(SO_4)_4 + 24H_2O$. The sesquioxides of nickel and cobalt on the other hand, act as peroxides, dissolving in acids with evolution of oxygen or chlorine. Manganese and iron likewise form salts which may be supposed to contain the trioxides MO_3, or in which the metal is sexvalent, analogous therefore in composition to the sulphates, *e.g.*, *potassium ferrate*, K_2FeO_4 or K_2O,FeO_3. Lastly, manganese forms a class of salts, the *permanganates*, *e.g.*, $KMnO_4$ or K_2O,Mn_2O_7, analogous in composition to the perchlorates, and isomorphous therewith ; in these salts the manganese must be supposed to be septivalent, like chlorine in the perchlorates.

MANGANESE.

Symbol, Mn. Atomic weight, 54·8.

Manganese is tolerably abundant in nature in the state of oxide, occurring chiefly as dioxide or pyrolusite, MnO_2 ; also as braunite, Mn_2O_3, and hausmannite, Mn_3O_4 ; and as carbonate in rhodochrosite or manganese spar, $MnCO_3$, which also occurs frequently as an isomorphous constituent in ferrous carbonate and other similar minerals. Manganese likewise enters, though only in small quantity, into the composition of many other minerals, and traces of it, derived from the soil, are often found in the ashes of plants.

Metallic manganese, or perhaps strictly, manganese carbonide, may be prepared by the following process :—The carbonate is calcined in an open vessel, by which it becomes converted into a dense brown powder : this is intimately mixed with a little charcoal, and about one-tenth of its weight of anhydrous borax. A charcoal crucible is next prepared by filling a Hessian or Cornish crucible

with moist charcoal powder, introduced a little at a time, and rammed as hard as possible. A smooth cavity is then scooped in the centre, into which the above-mentioned mixture is compressed, and covered with charcoal powder. The lid of the crucible is then fixed, and the whole arranged in a very powerful wind-furnace. The heat is slowly raised until the crucible becomes red hot, after which it is urged to its maximum for an hour or more. When cold, the crucible is broken up, and the metallic button of manganese extracted.

Deville has lately prepared pure manganese by reducing pure manganese oxide with an insufficient quantity of sugar-charcoal in a crucible made of caustic lime. Thus prepared, metallic manganese possesses a reddish lustre like bismuth: it is very hard and brittle, and, when powdered, decomposes water, even at the lowest temperature. Dilute sulphuric acid dissolves it with great energy, evolving hydrogen. Brunner produced metallic manganese from manganese and sodium fluoride by means of sodium. The metal obtained by this process scratches glass and hardened steel, and has a specific gravity of 7·13.

Manganese Chlorides.—The *dichloride*, or *Manganous chloride*, may be prepared in a state of purity from the dark brown liquid residue of the preparation of chlorine from manganese dioxide and hydrochloric acid, which often accumulates in the laboratory to a considerable extent: from the pure chloride, the carbonate and all the other salts can be conveniently obtained. The liquid referred to consists chiefly of the mixed chlorides of manganese and iron: it is filtered, evaporated to perfect dryness, and the residue is slowly heated to dull redness in an earthen vessel, with constant stirring. The iron chloride is thus either volatilised, or converted by the remaining water into insoluble sesquioxide, while the manganese salt is unaffected. On treating the greyish-looking powder thus obtained with water, the manganese chloride is dissolved out, and may be separated by filtration from the iron oxide. Should a trace of the latter yet remain, it may be got rid of by boiling the liquid for a few minutes with a little manganese carbonate. The solution of the chloride has usually a delicate pink colour, which becomes very manifest when the salt is evaporated to dryness. A strong solution deposits rose-coloured tabular crystals, which contain 4 molecules of water; they are very soluble and deliquescent. The chloride is fusible at a red heat, is decomposed slightly at that temperature by contact with air, and is dissolved by alcohol, with which it forms a crystallisable compound.

The *trichloride*, or *Manganic chloride*, Mn_2Cl_6, is formed when precipitated manganic oxide is immersed in cold concentrated hydrochloric acid, the oxide then dissolving quietly without evolution of gas. Heat decomposes the trichloride into dichloride and free chlorine.

Heptachloride, $MnCl_7$ (?).—When potassium permanganate is dis-

solved in strong sulphuric acid, and fused sodium chloride is added by small portions at a time, a greenish-yellow gas is given off, which condenses at 0° to a greenish-brown liquid. This compound, when exposed to moist air, gives off fumes, coloured purple by permanganic acid, and is instantly decomposed by water into permanganic and hydrochloric acids. It is regarded by Dumas, who discovered it, as the heptachloride of manganese; but H. Rose regarded it as an oxychloride, $MnCl_2O_3$, analogous to chromic oxychloride, a view which is in accordance with its mode of formation.

Fluorides of manganese have been formed analogous to each of these chlorides.

Manganese Oxides and Oxysalts.—Manganese forms four well-defined oxides, constituted as follows:—

Monoxide, or Manganous oxide	MnO
Trimangano-tetroxide, or Manganoso-manganic oxide	Mn_3O_4
Sesquioxide, or Manganic oxide	Mn_2O_3
Dioxide or Peroxide	MnO_2

The first is a strong base, the third a weak base; the second and fourth are neutral; the second may be regarded as a compound of the first and third, MnO,Mn_2O_3. There are also several oxides intermediate between the monoxide and dioxide, occurring as natural minerals or ores of manganese. Manganese likewise forms two series of oxygen-salts, called *manganates* and *permanganates*, the composition of which has been already noticed (p. 476). The oxides, MnO_3 and Mn_2O_7, corresponding with these salts, are not known.

Monoxide, or *Manganous oxide*, MnO.—When manganese carbonate is heated in a stream of hydrogen gas, or vapour of water, carbon dioxide is disengaged, and a greenish powder left behind, which is the monoxide. Prepared at a dull red heat only, the monoxide is so prone to absorb oxygen from the air, that it cannot be removed from the tube without change; but when prepared at a higher temperature, it appears more stable. This oxide is a very strong base, isomorphous with magnesia and zinc oxide; it dissolves quietly in dilute acids, neutralising them completely, and forming salts, which have often a beautiful pink colour. When alkalis are added to solutions of these compounds, the white hydrated oxide first precipitated speedily becomes brown by passing into a higher state of oxidation.

Sesquioxide, or *Manganic oxide*, Mn_2O_3.—This compound occurs in nature as *braunite*, and in the state of hydrate as *manganite:* a very beautiful crystallised variety is found at Ilefeld, in the Hartz. It is produced artificially, by exposing the hydrated monoxide to the air, and forms the principal part of the residue left in the iron retort when oxygen gas is prepared by exposing the native dioxide to a moderate red heat. The colour of the sesquioxide is brown or black, according to its origin or mode of preparation. It is a weak base, isomorphous with alumina: for when gently heated with

diluted sulphuric acid, it dissolves to a red liquid, which, on the addition of potassium or ammonium sulphate, deposits octohedral crystals having a constitution similar to that of common alum: these are, however, decomposed by water. Strong nitric acid resolves this oxide into a mixture of monoxide and dioxide, the former dissolving, and the latter remaining unaltered, while hot oil of vitriol decomposes it by forming manganous sulphate and liberating oxygen gas. On heating it with hydrochloric acid, chlorine is evolved, as with the dioxide, but in smaller amount.

Dioxide, MnO_2.—*Peroxide of Manganese. Pyrolusite.*—The most common ore of manganese; it is found both massive and crystallised. It may be obtained artificially in the anhydrous state by gently calcining the nitrate; or in combination with water, by adding solution of bleaching powder to a salt of the monoxide. Manganese dioxide has a black colour, and is insoluble in water. It is decomposed by hot hydrochloric acid and by oil of vitriol in the same manner as the sesquioxide. It unites with the stronger bases, potash, lime, &c., forming salts called manganites, *e.g.*, CaO,MnO_2 or $CaMnO_3$, which are produced by precipitating a solution of a manganous salt with the corresponding base in presence of an oxidising agent, such as a stream of air or oxygen gas. Such are the manganites of calcium and magnesium formed in Weldon's process for the recovery of manganese dioxide from waste chlorine-liquors (p. 141). According to Frémy,* manganese dioxide likewise acts as a base, forming definite salts with acids, *e.g.*, a sulphate, MnO_2,SO_3.

The proportion of real dioxide contained in a commercial sample of the black oxide may be estimated by determining the quantity of carbon dioxide evolved on gently heating a weighed quantity of oxalic acid, $C_2H_2O_4$, with strong hydrochloric acid in presence of a known weight of the manganese ore. The following reaction then takes place:

$$MnO_2 + C_2H_2O_4 + 2HCl = MnCl_2 + 2H_2O + 2CO_2.$$

This equation shows that every two molecules of carbon dioxide evolved correspond with one molecule of manganese dioxide decomposed. Now the molecular weight of this oxide, 87, is so nearly equal to twice that of carbon dioxide, 44, that the loss of weight suffered by the apparatus when the reaction has become complete, and the residual gas has been driven off by momentary ebullition, may be taken to represent the quantity of real dioxide in the 50 grains of the sample. Geissler's apparatus (p. 261) may be advantageously used in this process.

Trimangano-tetroxide, or *Red manganese oxide*, Mn_3O_4, or probably MnO,Mn_2O_3.—This oxide is also found native, as *hausmannite*, and is produced artificially by heating the dioxide or sesqui-

* Comptes rendus, lxxxii. 1231; Chem. Soc. Journ., 1877, i. 52.

oxide to whiteness, or by exposing the monoxide or carbonate to a red heat in an open vessel. It is a reddish-brown substance, incapable of forming salts, and acted upon by acids in the same manner as the two other oxides already described. Borax and glass in the fused state dissolve it, and acquire the colour of amethyst.

Varvicite, Mn_4O_7,H_2O or $MnO,3MnO_2,H_2O$, is a natural mineral discovered by Phillips among certain specimens of manganese ore from Warwickshire : it has also been found at Ilefeld in the Hartz. It much resembles the dioxide, but is harder and more brilliant. By a strong heat, varvicite is converted into red oxide, with disengagement of aqueous vapour and oxygen gas.

Several other oxides, intermediate in composition between the monoxide and dioxide, also occur native ; they are probably mere mixtures, and in many cases the monoxide is more or less replaced by the corresponding oxides of iron, cobalt, and copper.

Manganous Sulphate, $MnSO_4,7H_2O$ or $MnO,SO_3,7H_2O$.—A beautiful rose-coloured and very soluble salt, isomorphous with magnesium sulphate. It is prepared on the large scale for the use of the dyer, by heating in a close vessel manganese dioxide and coal, and dissolving the impure monoxide thus obtained in sulphuric acid, with addition of a little hydrochloric acid towards the end of the process. The solution is evaporated to dryness, and again exposed to a red heat, by which ferric sulphate is decomposed. Water then dissolves out the pure manganese sulphate, leaving ferric oxide behind. This salt is used to produce a permanent brown dye, the cloth steeped in the solution being afterwards passed through a solution of bleaching powder, by which the monoxide is changed to insoluble hydrate of the dioxide. Manganous sulphate sometimes crystallises with 5 molecules of water. It forms a double salt with potassium sulphate, containing $MnK_2(SO_4)_2,6H_2O$.

Manganous Carbonate, $MnCO_3$ or MnO,CO_2.—Prepared by precipitating the dichloride with an alkaline carbonate. It is an insoluble white powder, sometimes with a buff-coloured tint. Exposed to heat, it loses carbon dioxide and absorbs oxygen.

Manganates.—When an oxide of manganese is fused with potash, oxygen is taken up from the air, and a deep green saline mass results, which contains *potassium manganate*, K_2MnO_4 or K_2O,MnO_3. The addition of potassium nitrate or chlorate facilitates the reaction. Water dissolves this compound very readily, and the solution, concentrated by evaporation in a vacuum, yields green crystals. *Barium manganate*, $BaMnO_4$, is formed in a similar manner. In these salts manganese is sexvalent, like chromium in the chromates.

Permanganates.—When potassium manganate, free from any great excess of alkali, is put into a large quantity of water, it is re olved into hydrated manganese dioxide, which subsides, and

potassium permanganate, $K_2Mn_2O_8$ or K_2O,Mn_2O_7, which remains in solution, forming a deep purple liquid:

$$3K_2MnO_4 + 2H_2O = MnO_2 + K_2Mn_2O_8 + 4KHO.$$

This effect is accelerated by heat. The changes of colour accompanying this decomposition are very remarkable, and have procured for the manganate the name *mineral chameleon;* excess of alkali hinders the reaction in some measure, by conferring greater stability on the manganate. Potassium permanganate is easily prepared on a considerable scale. Equal parts of very finely powdered manganese dioxide and potassium chlorate are mixed with rather more than 1 part of potassium hydroxide dissolved in a little water, and the whole is exposed, after evaporation to dryness, to a temperature just short of ignition. The mass is treated with hot water, the insoluble oxide separated by decantation, and the deep-purple liquid concentrated by heat, until crystals form upon its surface: it is then left to cool. The crystals have a dark purple colour, and are not very soluble in cold water. The manganates and permanganates are decomposed by contact with organic matter. The green and red disinfecting agents, known as Condy's fluids, are alkaline manganates and permanganates.

Hydrogen Permanganate, or *Permanganic acid*, $H_2Mn_2O_8$, is obtained by dissolving potassium permanganate in hydrogen sulphate, H_2SO_4, diluted with 1 molecule of water, and distilling the solution at 60°—70°. Permanganic acid then passes over in violet vapours, and condenses to a greenish-black liquid, which has a metallic lustre, absorbs moisture greedily from the air, and acts as a most powerful oxidising agent, instantly setting fire to paper and to alcohol.

Manganous salts are very easily distinguished by reagents. The *fixed caustic alkalis* and *ammonia* give white precipitates, insoluble in excess, quickly becoming brown. The *carbonates of the fixed alkalis* and *carbonate of ammonia* give white precipitates, but little subject to change, and insoluble in excess of carbonate of ammonia. *Hydrogen sulphide* gives no precipitate, but *ammonium sulphide* throws down insoluble flesh-coloured sulphide of manganese, which is very characteristic. *Potassium ferrocyanide* gives a white precipitate.

Manganese is also easily detected by the blow-pipe: it gives with borax an amethyst-coloured bead in the outer or oxidising flame, and a colourless bead in the inner flame. Heated upon platinum foil with sodium carbonate, it yields a green mass of sodium manganate.

IRON.

Symbol, Fe (Ferrum). Atomic weight, 56.

This is the most important of all the metals: there are few substances to which it yields in interest, when we consider how very intimately the knowledge of its properties and uses is connected with human civilisation.

Metallic iron occurs but rarely on the earth, being found only at Canaan in Connecticut, where it forms a vein about two inches thick in mica-slate, and in a few other localities, but it enters into the composition of many *meteorites*. Isolated masses of soft malleable iron also, of large dimensions, lie loose upon the surface of the earth in South America, Greenland, and elsewhere, and are presumed to have had a similar origin: these latter, in common with the iron of the undoubted meteorites, contain nickel. In the state of oxide, the presence of iron may be said to be universal: it constitutes a great part of the common colouring matter of rocks and soils; it is contained in plants, and forms an essential component of the blood of the animal body. It is also very common in the state of bisulphide.

Pure iron may be prepared, according to Mitscherlich, by introducing into a Hessian crucible 4 parts of fine iron wire cut small, and 1 part of black iron oxide. This is covered with a mixture of white sand, lime, and potassium carbonate, in the proportions used for glass-making, and a cover being closely applied, the crucible is exposed to a very high degree of heat. A button of pure metal is thus obtained, the traces of carbon and silicon present in the wire having been removed by the oxygen of the oxide.

Pure iron has a white colour and perfect lustre: it is extremely soft and tough, and has a specific gravity of 7·8. Its crystalline form is probably the cube, to judge from appearances occasionally exhibited. In good bar-iron or wire, a distinct fibrous texture may always be observed when the metal has been attacked by rusting or by the application of an acid; and upon the perfection of this fibre much of its strength and value depends. Iron is the most tenacious of all the metals, a wire $\frac{1}{36}$ of an inch in diameter bearing a weight of 60 lbs. It is very difficult of fusion, and before becoming liquid passes through a soft or pasty condition. Pieces of iron, pressed or hammered together in this state, cohere into a single mass: this operation, termed *welding*, is usually performed by sprinkling a little sand over the heated metal, which combines with the superficial film of oxide, forming a fusible silicate, which is subsequently forced out from between the pieces of iron by the pressure applied: clean surfaces of metal are thus presented to each other, and union takes place without difficulty.

Iron does not oxidise in dry air at common temperatures: heated to redness, it becomes covered with a scaly coating of black oxide, and at a high white heat burns brilliantly, producing the same

substance. In oxygen gas the combustion occurs with still greater ease. The finely divided spongy metal, prepared by reducing the red oxide with hydrogen gas, takes fire spontaneously in the air. Pure water, free from air and carbonic acid, does not tarnish a surface of polished iron, but the combined agency of free oxygen and moisture speedily leads to the production of rust, which is a hydrate of the sesquioxide. The rusting of iron is wonderfully promoted by the presence of a little acid vapour. At a red heat, iron decomposes water, evolving hydrogen, and passing into the black oxide. Dilute sulphuric and hydrochloric acids dissolve it freely, with separation of hydrogen. Iron is strongly magnetic up to a red heat, but at that temperature it loses all traces of magnetism.

Iron forms two classes of compounds: namely the ferrous compounds, in which it is bivalent, *e.g.*, $FeCl_2$, FeO, $FeSO_4$, &c., and the ferric compounds, in which, like aluminium, it may be regarded either as a triad or as a tetrad: ferric chloride, for example, may be either $FeCl_3$ or $Fe_2Cl_6 = Cl_3Fe.FeCl_3$; the vapour-density of this compound, as determined by Deville, is in favour of the latter formula.

Chlorides.—The *dichloride*, or *Ferrous chloride*, $FeCl_2$, is formed by transmitting dry hydrochloric acid gas over red-hot metallic iron, or by dissolving iron in hydrochloric acid. The latter solution yields, when duly concentrated, green crystals of the hydrated dichloride, $FeCl_2.4H_2O$; they are very soluble and deliquescent, and oxidise rapidly in the air.

The *trichloride* or *Ferric chloride*, Fe_2Cl_6, is usually prepared by dissolving ferric oxide in hydrochloric acid. The solution, evaporated to a syrupy consistence, deposits red hydrated crystals, which are very soluble in water and alcohol. It forms double salts with potassium chloride and sal-ammoniac. When evaporated to dryness and strongly heated, much of the chloride is decomposed, yielding sesquioxide and hydrochloric acid: the remainder sublimes, and afterwards condenses in the form of small brilliant red crystals, which deliquesce rapidly. Anhydrous ferric chloride is also produced by the action of chlorine upon the heated metal. The solution of ferric chloride is capable of dissolving a large excess of recently precipitated ferric hydroxide, by which it acquires a much darker colour.

Iodides.—*Ferrous iodide*, FeI_2, is an important medicinal preparation: it is easily made by digesting iodine with water and metallic iron. The solution is pale-green, and yields, on evaporation, crystals resembling those of the chloride, which rapidly oxidise on exposure to air. It is best preserved in solution in contact with excess of iron.—*Ferric iodide*, Fe_2I_6, is yellowish-red and soluble.

Iron Oxides and Oxysalts.—Three oxides of iron are known, namely, ferrous oxide, FeO, and ferric oxide, Fe_2O_3, analogous to

the chlorides, and an intermediate oxide, usually called magnetic iron oxide, containing Fe_3O_4 or FeO,Fe_2O_3. A trioxide, FeO_3, may be supposed to exist in the ferrates, but it has not been isolated.

Monoxide, or *Ferrous oxide*, FeO.—This is a very powerful base, neutralising acids, and isomorphous with magnesia, zinc oxide, &c. It is almost unknown in the separate state, from its extreme proneness to absorb oxygen and pass into the sesquioxide. When a ferrous salt is mixed with caustic alkali or ammonia, a bulky whitish precipitate of ferrous hydroxide falls, which becomes nearly black when boiled, the water being separated. This hydroxide changes very rapidly when exposed to the air, becoming green and ultimately red-brown. The soluble ferrous salts have commonly a delicate pale-green colour and a nauseous metallic taste.

Sesquioxide, or *Ferric oxide*, Fe_2O_3.—A weak base, isomorphous with alumina. It occurs native, most beautifully crystallised, as specular iron ore, in the island of Elba, and elsewhere ; also as red and brown *hæmatite*, the latter being a hydrate. It is artificially prepared by precipitating a solution of ferric sulphate or chloride with excess of ammonia, and washing, drying, and igniting the yellowish-brown hydrate thus produced : fixed alkali must not be used in this operation, as a portion is retained by the oxide. In fine powder, this oxide has a full red colour, and is used as a pigment, being prepared for the purpose by calcination of ferrous sulphate ; the tint varies somewhat with the temperature to which it has been exposed. The oxide is unaltered in the fire, although easily reduced at a high temperature by carbon or hydrogen. It dissolves in acids, with difficulty after strong ignition, forming a series of reddish salts, which have an acid reaction and an astringent taste. Ferric oxide is not acted upon by the magnet.

Triferro-tetroxide, *Ferroso-ferric oxide*, $Fe_3O_4 = FeO,Fe_2O_3$, also called *black iron oxide*, *magnetic oxide*, and *loadstone*, occurs as a natural product, one of the most valuable of the iron-ores, and is often found in regular octohedral crystals, which are magnetic. It may be prepared by mixing due proportions of ferrous and ferric salts, precipitating them with excess of alkali, and then boiling the mixed hydroxides ; the latter then unite to a black sandy substance, consisting of minute crystals of the magnetic oxide. This oxide is the chief product of the oxidation of iron at a high temperature in the air and in aqueous vapour.

Ferrates.—When a mixture of one part of pure ferric oxide and four parts of dry nitre is heated to full redness for an hour in a covered crucible, and the resulting brown, porous, deliquescent mass is treated when cold with ice-cold water, a deep amethystine-red solution of potassium ferrate is obtained. The same salt may be more easily prepared by passing chlorine gas through a strong solution of potash in which recently precipitated ferric hydroxide is suspended ; it is then deposited as a black powder, which may be drained upon a tile. It consists of K_2FeO_4 or K_2O,FeO_3, and is

therefore analogous in composition to the sulphate and chromate of potassium. The solution of this salt gradually decomposes, even in the cold, and rapidly when heated, giving off oxygen and depositing sesquioxide. The solution of potassium ferrate gives no precipitate with salts of calcium, magnesium, or strontium, but when mixed with a barium salt, it yields a deep crimson, insoluble *barium ferrate*, $BaFeO_4$ or BaO,FeO_3, which is very permanent. Neither the hydrogen-salt or ferric acid, H_2FeO_4, nor the corresponding anhydrous oxide, FeO_3, is known in the separate state.

Ferrous Sulphate, $FeSO_4,7H_2O$ or $FeO,SO_3,7H_2O$. — This beautiful and important salt, commonly called *green vitriol*, *iron vitriol*, or *copperas*, may be obtained by dissolving iron in dilute sulphuric acid : it is generally prepared, however, and on a very large scale, by contact of air and moisture with common iron pyrites, which, by absorption of oxygen, readily furnishes the substance in question. Heaps of this material are exposed to the air until the decomposition is sufficiently advanced: the salt produced is then dissolved out by water, and the solution is left to crystallise. It forms large green crystals, of the composition above stated, which slowly effloresce and oxidise in the air: it is soluble in about twice its weight of cold water. Crystals containing 4 and also 2 molecules of water have been obtained. Ferrous sulphate forms double salts with the sulphates of potassium and ammonium, containing $FeK_2(SO_4)_2,6H_2O$ and $Fe(NH_4)_2(SO_4)_2,6H_2O$, isomorphous with the corresponding magnesium salts.

Ferric Sulphate, $Fe_2(SO_4)_3$ or $Fe_2O_3,3SO_3$, is prepared by adding to a solution of the ferrous salt exactly one-half as much sulphuric acid as it already contains, raising the liquid to the boiling-point, and then dropping in nitric acid until the solution ceases to blacken by such addition. The red liquid thus obtained furnishes on evaporation to dryness, a buff-coloured amorphous mass, which dissolves very slowly when put into water. With the sulphates of potassium and ammonium, this salt yields compounds having the form and constitution of alums; the potassium salt, for example, has the composition $Fe''K(SO_4)_2,12H_2O$. The crystals are nearly colourless; they are decomposed by water, and sometimes by long keeping in the dry state. These iron-alums are best prepared by exposing to spontaneous evaporation a solution of ferric sulphate to which potassium or ammonium sulphate has been added.

Ferrous Nitrate, $Fe(NO_3)_2$.—When dilute cold nitric acid is made to act to saturation upon iron monosulphide, and the solution is evaporated in a vacuum, pale-green and very soluble crystals of ferrous nitrate are obtained, which are very subject to alteration. *Ferric nitrate* is readily formed by pouring nitric acid, slightly diluted, upon iron: it is a deep-red liquid, apt to deposit an insoluble basic salt, and is used in dyeing.

Ferrous Carbonate, $FeCO_3$ or FeO,CO_2, is obtained as a whitish precipitate on mixing solutions of ferrous salt and alkaline carbonate: it cannot be washed and dried without losing carbonic acid and absorbing oxygen. This compound occurs in nature as *spathose iron ore* or *iron spar*, associated with variable quantities of calcium and magnesium carbonates; also in the common *clay ironstone*, from which nearly all the British iron is made. It is often found in mineral waters, being soluble in excess of carbonic acid: such waters are known by the rusty matter they deposit on exposure to the air. No ferric carbonate is known.

The *phosphates* of iron are all insoluble.

Iron Sulphides.—Several compounds of iron and sulphur are known: of these the two most important are the following. The *monosulphide*, or *ferrous sulphide*, FeS, is a blackish brittle substance, attracted by the magnet, formed by heating together iron and sulphur. It is dissolved by dilute acids, with evolution of sulphuretted hydrogen gas, and is constantly employed for that purpose in the laboratory, being made by projecting into a red-hot crucible a mixture of $2\frac{1}{2}$ parts of sulphur and 4 parts of iron filings or borings of cast iron, and excluding the air as much as possible. The same substance is formed when a bar of white-hot iron is brought in contact with sulphur. The *bisulphide*, FeS_2, or iron pyrites, is a natural product, occurring in rocks of all ages, and evidently formed in many cases by the gradual deoxidation of ferrous sulphate by organic matter. It has a brass-yellow colour, is very hard, not attracted by the magnet, and not acted upon by dilute acids. When it is exposed to heat, sulphur is expelled, and an intermediate sulphide, Fe_3S_4, analogous to the black oxide, is produced. This latter substance also occurs native, under the name of *magnetic pyrites*. Iron pyrites is the material now chiefly employed for the manufacture of sulphuric acid; for this purpose the mineral is roasted in a current of air, and the sulphurous acid formed is passed into the lead chambers; the residue consists of iron oxide, frequently containing a quantity of copper large enough to render the extraction of that metal remunerative.

Compounds of iron with *phosphorus*, *carbon*, and *silicon*, exist, but little is known respecting them in a definite state. The carbonide is contained in cast iron and in steel, to which it communicates ready fusibility; the silicon-compound is also found in cast iron. Phosphorus is a very hurtful substance in bar iron, rendering it brittle or *cold-short*.

Reactions of Iron Salts.—Ferrous salts are thus distinguished.

Caustic alkalis and *ammonia* give nearly white precipitates, insoluble in excess of the reagent, rapidly becoming green, and ultimately brown, by exposure to air. The *carbonates* of *potassium*,

sodium, and *ammonium* throw down whitish ferrous carbonate, also very subject to change. *Hydrogen sulphide* gives no precipitate, but *ammonium sulphide* throws down black ferrous sulphide, soluble in dilute acids. *Potassium ferrocyanide* gives a nearly white precipitate, becoming deep-blue on exposure to air; the *ferricyanide* gives at once a deep-blue precipitate.

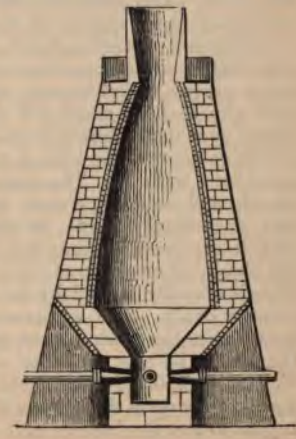
Ferric salts are thus characterised:

Caustic fixed alkalis and *ammonia* give foxy-red precipitates of ferric hydrate, insoluble in excess. The *carbonates* behave in a similar manner, the carbonic acid escaping. *Hydrogen sulphide* gives a nearly white precipitate of sulphur, and reduces the sesquioxide to monoxide. *Ammonium sulphide* gives a black precipitate, slightly soluble in excess. *Potassium ferrocyanide* yields Prussian blue. Tincture or infusion of *gall-nuts* strikes a deep bluish-black with the most dilute solutions of ferric salts.

Iron Manufacture.—This most important branch of industry consists, as now conducted, of two distinct parts—viz., the production from the ore of a fusible carbonide of iron, and the subsequent decomposition of the carbonide, and its conversion into pure or malleable iron.

Clay-iron ore is found in association with coal, forming thin beds or nodules: it consists, as already mentioned, of ferrous carbonate mixed with clay; sometimes lime and magnesia are also present. It is broken in pieces, and exposed to heat in a furnace resembling a lime-kiln, by which the water and carbonic acid are expelled, and the ore is rendered dark-coloured, denser, and magnetic: it is then ready for reduction. The furnace in which this operation is performed is usually of very large dimensions, 50 feet or more in height, and constructed of very solid brickwork, the interior being lined with excellent fire-bricks. A general idea of the shape may be gained from the section shown in fig. 150. In modern blast-furnaces, however, the sides of the shaft are nearly vertical, and the lower part, called the *hearth*, is proportionally wider than in the figure. The furnace is closed at the bottom, the fire being maintained by a powerful artificial blast introduced by two or three *twyere-pipes*. The materials, consisting of due

Fig. 150.



proportions of coke or coal, roasted ore, and limestone, are constantly supplied from the top, the operation proceeding continuously night and day, often for years, or until the furnace is judged to require repair. In the upper part or shaft of the furnace, where the temperature is still very high, and where combustible gases abound, the iron of the ore is probably reduced to the metallic state, being disseminated through the earthy matter of the ore. As the whole sinks down and attains a still higher degree of heat, the iron becomes converted into carbonide by *cementation*, while the silica and alumina unite with the lime, purposely added, forming a kind of glass or *slag*, nearly free from iron oxide. The carbonide and slag, both in the melted state, reach at last the bottom or hearth of the furnace, where they arrange themselves in the order of their densities. The slag flows out at certain apertures contrived for the purpose, and the iron is discharged from time to time, and suffered to run into rude moulds of sand by opening an orifice at the bottom of the recipient, previously stopped with clay. Such is the origin of *crude*, *cast*, or *pig iron*, of which there are several varieties, distinguished by differences of colour, hardness, and composition, and known by the names of *grey*, *black*, and *white* iron. The first is for most purposes the best, as it admits of being filed and cut with perfect ease. The black and grey kinds probably contain a mechanical admixture of graphite, which separates during solidification.

A great improvement in the original mode of conducting the process was the substitution of raw coal for coke, and the blowing of hot air instead of cold into the furnace. This is effected by causing the air, on leaving the blowing-machine, to circulate through a system of red-hot iron pipes, until its temperature becomes high enough to melt lead. This alteration effects a prodigious saving in fuel, without injury to the quality of the product.

The conversion of cast into bar iron is effected chiefly by an operation called *puddling*, previous to which, however, it sometimes undergoes a process called *refining*, which consists in remelting it, in contact with the fuel, in small low furnaces called *refineries*, while air is blown over its surface by means of twyeres. The effect of this operation is to deprive the iron of a great part of the carbon and silicon associated with it. The metal thus purified is run out into a trench, and suddenly cooled, by which it becomes white, crystalline, and exceedingly hard: in this state it is called *fine metal*. The *puddling* process is conducted in a reverberatory furnace, into which the charge of crude or of fine metal is introduced by a side aperture. This is speedily melted by the flame, and its surface covered with a crust or oxide. The workman then, by the aid of an iron tool, diligently stirs the melted mass, so as intimately to mix the oxide with the metal; he now and then also throws in a little water, with the view of promoting more rapid oxidation. Small jets of blue flame soon appear upon the surface of the iron, and the latter, after a time, begins to lose its fluidity, and acquires, in succession, a pasty and a

granular condition. At this point the fire is strongly urged, the sandy particles once more cohere, and the contents of the furnace now admit of being formed into several large balls or masses, which are then withdrawn, and placed under an immense hammer, moved by machinery, by which each becomes quickly fashioned into a rude bar. This is reheated, and passed between grooved cast iron rollers, and drawn out into a long bar or rod. To make the best iron, the bar is cut into a number of pieces, which are afterwards piled or bound together, again raised to a welding heat, and hammered or rolled into a single bar; and this process of *piling* or *fagotting* is sometimes twice or thrice repeated, the iron becoming greatly improved thereby.

The general nature of the change in the puddling furnace is not difficult to explain. Cast iron consists essentially of iron in combination with carbon and silicon, and these compounds, when strongly heated with iron oxide, undergo decomposition, the carbon and silicon becoming oxidised at the expense of the oxygen of the oxide. As this change takes place, the metal gradually loses its fusibility, but retains a certain degree of adhesiveness, so that when at last it comes under the tilt-hammer, or between the rollers, the particles of iron become agglutinated into a solid mass, while the readily fusible silicate of the oxide is squeezed out and separated.

All these processes are, in Great Britain, performed with coal or coke; but the iron obtained is, in many respects, inferior to that made in Sweden and Russia from the magnetic oxide, by the use of wood charcoal—a fuel too dear to be extensively employed in England. Plate iron is, however, sometimes made with charcoal.

A method of producing malleable iron directly from the ore has been invented by C. W. Siemens.* The furnace consists of a rotatory iron cylinder, which, by means of wheel-gearing, may be made to revolve either four or five times or from 60 to 80 times in an hour. The ore to be smelted is broken into fragments not exceeding the size of peas or beans; and to it is added lime or other fluxing material, in such proportion that the gangue contained in the ore and flux combines with only a little ferrous oxide into basic and fluid slag. If the ore is hæmatite, or contains silica, it is best to add alumina in the shape of aluminous iron ore; manganiferous iron ore may also be added with advantage. A charge of about 20 cwts. of ore is put into the furnace when fully heated, while it is revolving slowly. In about forty minutes this charge of ore and fluxing material will have been heated to bright redness, and at this time from 5 to 6 cwts. of small coal of uniform size (not larger than nuts) is added to the charge, whilst the rotative velocity is increased in order to accelerate the mixture of coal and ore. A quick reaction follows: the ferric oxide being reduced to magnetic

* Chem. Soc. Jour., 1874, p. 671; Watts's Dictionary of Chemistry, 2nd Suppl., p. 701.

oxide begins to fuse, and at the same time metallic iron is precipitated by each piece of carbon, while the fluxing materials form a fluid slag with the siliceous gangue of the ore. The slow rotative action is then again resorted to, whereby the mass is turned over and over, presenting continually new surfaces to the heated lining and to the flame within the rotator.

When the reduction of the iron ore is nearly completed, the rotator is stopped in the proper position for tapping off the fluid cinder; after this the quick speed is imparted to the rotator, whereby the loose masses of iron contained in it are rapidly collected into two or three metallic balls. These are taken out and shingled in the usual way of consolidating puddled balls; the furnace is tapped again, and is ready to receive another charge of ore.

Steel is prepared by heating iron in contact with charcoal. Bars of Swedish iron are imbedded in charcoal powder, contained in a large rectangular crucible or chest of some substance capable of resisting the fire, and exposed for many hours to a full red heat. The iron takes up, under these circumstances, from 1·3 to 1·7 per cent. of carbon, becoming harder, and at the same time fusible, but with a certain diminution of malleability. The active agent in this cementation process is probably carbon monoxide: the oxygen of the air in the crucible unites with the carbon to form that compound, which is afterwards decomposed by the heated iron, one-half of its carbon being abstracted by the latter. The carbon dioxide thus formed takes up an additional dose of carbon from the charcoal, and again becomes monoxide, the oxygen, or rather the carbon dioxide, acting as a carrier between the charcoal and the metal. The product of this operation is called *blistered* steel, from the blistered and rough appearance of the bars: the texture is afterwards improved and equalised by welding a number of these bars together, and drawing the whole out under a light tilt-hammer.

Some chemists have recently asserted that nitrogen is necessary for the production of steel, and have, in fact, attributed to its presence the peculiar properties of this material; others, again, have disputed this assertion, and believe that the transformation of iron into steel depends upon the assimilation of carbon only; experimentally, the question remains undecided.

Excellent steel is obtained by fusing grey cast iron with tungstic oxide; the carbon of the iron reduces the tungstic oxide to tungsten, which forms with the iron an alloy possessing the properties of steel. The quantity of tungsten thus absorbed by the iron is very small, and some chemists attribute the properties of the so-called tungsten-steel to the general treatment rather than to the presence of tungsten.

The most perfect kind of steel is that which has undergone fusion, having been cast into ingot-moulds, and afterwards hammered: of this all fine cutting instruments are made. It is difficult to forge, requiring great skill and care on the part of the operator.

Steel may also be made directly from some particular varieties of cast iron, as that from spathose iron ore containing a little manganese. The metal is retained, in a melted state, on the hearth of a furnace, while a stream of air plays upon it, and causes partial oxidation: the oxide produced reacts, as before stated, on the carbon of the iron, and withdraws a portion of that element. When a proper degree of stiffness or pastiness is observed in the residual metal, it is withdrawn, and hammered or rolled into bars. The *wootz*, or native steel of India, is probably made in this manner. Annealed cast iron, sometimes called *run steel*, is now much employed as a substitute for the more costly products of the forge: the articles when cast, are imbedded in powdered iron ore, or some earthy material, and, after being exposed to a moderate red heat for some time, are allowed to cool slowly, by which a very great degree of softness and malleability is attained. It is possible that some little decarbonisation may take place during this process.

Cast steel may also be made in Siemens's rotatory furnace above described, the balls being transferred from the rotator to the bath of a steel-melting furnace in their heated condition, and without subjecting them to previous consolidation under a hammer or shingling machine. It is possible, however, to push the operation within the rotator to the point of obtaining cast steel. For this purpose the relative amount of carbonaceous matter is somewhat increased in the first instance, so that the ball, if shingled, would be of the nature of puddled steel, or even contain some carbon mechanically mixed.

Bessemer steel is produced by forcing atmospheric air into melted cast iron. The carbon, being oxidised more readily than the iron, is converted into carbon monoxide, which escapes in a sufficiently heated state to take fire on coming in contact with the air. Considerable heat is generated by the oxidation of the carbon and iron, so that the temperature is kept above the melting point of steel during the whole of the operation. When the decarburation has been carried far enough, the current of air is stopped, and a small quantity of white pig-iron, containing a large amount of manganese, is dropped into the liquid metal. This serves to facilitate the separation of any gas retained within the melted metal, which, after a few minutes' rest, is run into ingot moulds.

Another method of steel-making is that known as the Siemens-Martin process, which consists in dissolving scrap-iron in molten pig-iron heated in a reverberatory furnace*.

The most remarkable property of steel is that of becoming exceedingly hard when quickly cooled. When heated to redness, and suddenly quenched in cold water, steel, in fact, becomes capable of

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* See Journal of the Chemical Society, 1868, pp. 278—310; Roscoe and Schorlemmer's Treatise on Chemistry, vol. 2, part ii. p. 77; Watts's Dictionary of Chemistry, vol. vi. p. 736.

scratching glass with facility: if reheated to redness, and once more left to cool slowly, it again becomes nearly as soft as ordinary iron; and between these two conditions, any required degree of hardness may be attained. The articles, forged into shape, are first hardened in the manner described; they are then *tempered*, or *let down*, by exposure to a proper degree of annealing heat, which is often judged of by the colour of the thin film of oxide which appears on the polished surface. Thus, a temperature of about 221° C. (430° F.), indicated by a faint straw colour, gives the proper temper for razors; that for scissors, penknives, &c., is comprised between 243° and 254° C. (470–490° F.), and is indicated by a full yellow or brown tint. Swords and watchsprings require to be softer and more elastic, and must be heated to 288° or 293° C. (550–560° F.), or until the surface becomes deep blue. Attention to these colours has now become of less importance, as metal baths are often substituted for the open fire in this operation.

COBALT.

Symbol, Co. Atomic weight, 58·8.

This metal occurs in combination with sulphur in linnæite, Co_3S_4; with arsenic in skutterudite, $CoAs_3$; with sulphur and arsenic in speiss-cobalt, $(Co,Ni,Fe)As_2$, and cobalt-glance, $(Co,Fe)(AsS)_2$; as arsenate in erythrin or cobalt-bloom, $Co_3(AsO_4)_2,8H_2O$; and associated with manganese in earthy cobalt or wad,

$$(Co,Mn)O,2MnO_2,4H_2O.$$

It is an almost invariable constituent of meteoric iron, and has been detected spectroscopically in the atmosphere of the sun.

Cobalt-compounds may be prepared from speiss or any arsenical cobalt-ore by the following process:—The mineral is broken into small fragments, mixed with from one-fourth to half its weight of iron filings, and the whole is dissolved in nitro-muriatic acid. The solution is gently evaporated to dryness, the residue treated with boiling water, and the insoluble iron arsenate removed by a filter The liquid is then acidulated with hydrochloric acid, treated with hydrogen sulphide in excess, which precipitates the copper, and after filtration, boiled with a little nitric acid to bring back the iron to the state of sesquioxide. To the cold and largely diluted liquid solution, acid sodium carbonate is gradually added, by which the ferric oxide may be completely separated without loss of nickel-salt. Lastly, the filtered solution, boiled with sodium carbonate in excess, yields an abundant precipitate of cobalt carbonate, more or less mixed with nickel carbonate.

The separation of cobalt from nickel is by no means easy, but is best effected by the following process, devised by H. Rose. The mixed carbonates having been dissolved in excess of hydro-

chloric acid, the solution, largely diluted with water, is supersaturated with chlorine gas, whereby the cobalt monoxide is converted into sesquioxide, while the nickel monoxide remains unaltered. The liquid is next mixed with excess of recently precipitated barium carbonate, left at rest for twelve to eighteen hours, and shaken up from time to time. The whole of the cobalt is thereby thrown down as sesquioxide, while the nickel remains in solution. The precipitate, consisting of cobalt sesquioxide mixed with barium carbonate, is then boiled with hydrochloric acid, in order to reduce the cobalt sesquioxide to monoxide, and dissolve it as chloride together with the barium. The latter metal is precipitated by sulphuric acid, and from the filtered liquid the cobalt may be precipitated as hydroxide by potash. A solution of cobalt free from the nickel may also be obtained by precipitating the mixed solution with oxalic acid: the whole of the nickel is thereby precipitated, together with a small portion of the cobalt, leaving pure cobalt in solution.*

Cobalt is a white, brittle, very tenacious metal, having a specific gravity of 8·5, and a very high melting point. It is unchanged in the air, and but feebly attacked by dilute hydrochloric and sulphuric acids. It is strongly magnetic.

Cobalt forms two classes of salts, analogous in composition to the ferrous and ferric salts; but the cobaltic salts, in which the metal is apparently trivalent, are very unstable.

Chlorides.—The *dichloride* or *Cobaltous chloride*, $CoCl_2$, is easily prepared by dissolving the oxide in hydrochloric acid; or it may be prepared directly from *cobalt-glance*, the native arsenide, by the process above described. It forms a deep rose-red solution, which, when sufficiently strong, deposits hydrated crystals of the same colour; when the liquid is evaporated by heat to a very small bulk, it deposits anhydrous crystals, which are blue: these latter by contact with water again dissolve to a red liquid. A dilute solution of cobalt chloride constitutes the well-known *blue sympathetic ink:* characters written on paper with this liquid are invisible, from their paleness of colour, until the salt has been rendered anhydrous by exposure to heat, when the letters appear blue. On laying it aside, moisture is absorbed, and the writing once more disappears. Green sympathetic ink is a mixture of the chlorides of cobalt and nickel.

The *trichloride*, or *Cobaltic chloride*, Co_2Cl_6, is obtained in solution by dissolving the sesquioxide in hydrochloric acid, and in small quantity by saturating a solution of the dichloride with chlorine gas. The liquid has a dark-brown colour, but easily decomposes, giving off chlorine and leaving the rose-coloured dichloride.

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* For other methods of separating cobalt and nickel, see Gmelin's Handbook, English edition, v. 355—360, and Watts's Dictionary of Chemistry, i. 1046.

Oxides and **Oxysalts.**—Cobalt forms a monoxide and a sesquioxide, also two or three oxides of intermediate composition, but not very well defined. The *monoxide*, or *Cobaltous oxide*, CoO, is a grey powder, very soluble in acids, and is a strong base, isomorphous with magnesia, affording salts of a fine red tint. It is prepared by precipitating cobaltous sulphate or chloride with sodium carbonate, and washing, drying, and igniting the precipitate. When the cobalt solution is mixed with caustic potash, a beautiful blue precipitate falls, which, when heated, becomes violet, and at length dirty red, from absorption of oxygen and a change in the state of hydration.

The *sesquioxide*, or *Cobaltic oxide*, Co_2O_3, is a black, insoluble, neutral powder, obtained by mixing solutions of cobalt and chloride of lime. It dissolves in acids, yielding the cobaltic salts.

Cobaltoso-cobaltic oxide, Co_3O_4, analogous to the magnetic oxide of iron, is formed when cobaltous nitrate or oxalate, or hydrated cobaltic oxide, is heated in contact with the air. According to Frémy, it is a salifiable base.

Another oxide, of acid character, is said to be obtained in the form of a potassium salt by fusing the monoxide or sesquioxide with potassium hydroxide. A crystalline salt is thus formed, consisting, according to Schwarzenberg, of $K_2O,3Co_3O_4,3H_2O$.

Cobaltous Salts.—The *sulphate*, $CoSO_4,7H_2O$, forms red crystals, requiring for solution 24 parts of cold water: they are identical in form with those of magnesium sulphate. It combines with the sulphates of potassium and ammonium, forming double salts containing 6 molecules of water.

A solution of oxalic acid added to cobaltous sulphate occasions, after some time, the separation of nearly the whole of the base in the state of oxalate.

The *carbonate* is thrown down by the alkaline carbonates from solutions of cobalt, as a pale peach-blossom-coloured precipitate of combined carbonate and hydroxide, containing $2CoCO_3,3CoH_2O_2 + H_2O$.

Cobaltic Salts.—Cobaltic oxide is a weak base, dissolving in cold acids, and forming brown solutions which are easily decomposed, the oxy-salts evolving oxygen and the chloride evolving chlorine. The most stable of these salts is the *acetate*, the solution of which gives brown precipitates with alkalis and sodium phosphate, and a black precipitate with ammonium sulphide.

Greater stability is exhibited by certain double cobaltic salts, the most important of which is:

Potassio-cobaltic Nitrite, $K_6Co_2(NO_2)_{12},3H_2O$, which is obtained as a yellow precipitate on adding potassium nitrite to the solution of a cobaltous salt, the chloride for example, acidulated with acetic acid, the reaction being represented by the equation:—

$$2CoCl_2 + 10KNO_2 + 4HNO_2 = K_6Co_2(NO_2)_{12} + 4KCl + N_2O_2 + 2H_2O.$$

This compound, called *Cobalt-yellow*, is a bright yellow powder composed of microscopic pyramids or stellate forms. It is usually anhydrous, but may be obtained, according to the strength of the solution, with 1 to 4 molecules of water, its colour then varying from bright yellow to a dark greenish-yellow. It is decomposed by nitric and hydrochloric acids, with aid of heat, slowly by caustic potash, but quickly by caustic soda or baryta at a gentle heat, yielding a precipitate of brown cobaltic hydroxide. When suspended in water, it is slowly attacked by hydrogen sulphide, quickly by ammonium sulphide, with formation of black cobalt sulphide. Corresponding double salts are also known, containing sodium, ammonium, and thallium.

Ammoniacal Cobalt Compounds.—Cobaltous salts, treated with ammonia in a vessel protected from the air, unite with the ammonia, forming compounds which may be called ammonio-cobaltous salts. Most of them contain 6 molecules of ammonia to 1 molecule of the cobalt-salt; thus the chloride contains $CoCl_2,6NH_3 + H_2O$; the nitrate, $Co(NO_3)_2 6NH_3 + 2H_2O$. They are generally crystallisable, and of a rose-colour, soluble without decomposition in ammonia, but decomposed by water, with formation of a basic salt. H. Rose, by treating dry cobalt chloride with ammonia gas, obtained the compound $CoCl_2,4NH_3$; and in like manner an ammonio-sulphate has been formed containing $CoSO_4,6NH_3$.

When an ammoniacal solution of cobalt is exposed to the air, oxygen is absorbed, the liquid turns brown, and new salts are formed, containing a higher oxide of cobalt (either Co_2O_3, or CoO_2), and therefore designated generally as peroxidised ammonio-cobalt salts. Several of them, containing different bases, are often formed at the same time. Most of the peroxidised ammonio-cobalt salts are composed of cobaltic salts united with two or more molecules of ammonia. The composition of the normal salts may be illustrated by the chlorides, as in the following table:—

Tetrammonio-cobaltic chloride . .	$Co_2Cl_6(NH_3)_4$
Hexammonio-cobaltic chloride . .	$Co_2Cl_6(NH_3)_6$
Octammonio-cobaltic (or praseo-cobaltic) chloride	$Co_2Cl_6(NH_3)_8$
Decammonio-cobaltic (roseo- and purpureo-cobaltic) chloride . . .	$Co_2Cl_6(NH_3)_{10}$
Dodecammonio-cobaltic (or luteo-cobaltic) chloride	$Co_2Cl_6(NH_3)_{12}$

The formulæ of the corresponding normal nitrates are deduced from the preceding by substituting NO_3 for Cl; those of the sulphates, oxalates, and other bibasic salts, by substituting SO_4, C_2O_4, &c., for Cl_2, *e.g. decammonio-cobaltic sulphate* $= Co_2(SO_4)_3(NH_3)_{10}$. There are also acid and basic salts of the same ammonia-molecules, such as the *oxyoctammonio-cobaltic* or *fusco-cobaltic salts*, which may be regarded as basic praseo-cobaltic salts, *e.g.*, the *hydroxynitrate*,

$Co_2(NO_3)_4(OH)_2(NH_3)_8$. Further, there are salts containing the radicles NO and NO_2, in addition to ammonia, *e.g.*, *decammonio-nitroso-cobaltic* or *xantho-cobaltic chloride*, $Co_2Cl_4(NO_2)_2(NH_3)_2$, which may be regarded as roseo- or purpureo-cobaltic salts, in which one-third of the chlorine or other acid radicle is replaced by NO_2. Lastly, Frémy has obtained ammoniacal compounds (*oxycobaltic salts*) containing salts of cobalt corresponding with the dioxide.*

Cobaltous salts have the following characters:—

Solution of *potash* gives a blue precipitate, changing by heat to violet and red. *Ammonia* gives a blue precipitate, soluble with difficulty in excess, with brownish-red colour. *Sodium carbonate* forms a pink precipitate. *Ammonium carbonate*, a similar compound, soluble in excess. *Potassium ferrocyanide* gives a greyish-green precipitate. *Potassium cyanide* forms a yellowish-brown precipitate, which dissolves in an excess of the precipitant. The clear solution, after boiling, may be mixed with hydrochloric acid without giving a precipitate. *Hydrogen sulphide* produces no change, if the cobalt is combined with a strong acid. *Ammonium sulphide* throws down black sulphide of cobalt, insoluble in dilute hydrochloric acid.

Cobaltic salts, formed by dissolving cobaltic oxide in acids, give, with *potash*, a dark-brown precipitate of hydrated cobaltic oxide; with ammonia, a brownish-red solution; with the *fixed alkaline carbonates*, a green solution, which deposits a small quantity of cobaltic oxide; with *ammonium sulphide* (after saturation of the free acid by ammonia), a black precipitate.

Oxide of cobalt is remarkable for the magnificent blue colour it communicates to glass: indeed, this is a character by which its presence may be most easily detected, a very small portion of the substance to be examined being fused with borax on a loop of platinum wire before the blowpipe; the production of this colour both in the inner and in the outer flame distinguishes cobalt from all other metals.

The substance called *smalt*, used as a pigment, consists of glass coloured by cobalt: it is thus made:—The cobalt ore is roasted until nearly free from arsenic, and then fused with a mixture of potassium carbonate and quartz-sand, free from oxide of iron. Any nickel that may happen to be contained in the ore then subsides to the bottom of the crucible as arsenide: this is the *speiss* already mentioned. The glass, when complete, is removed and poured into cold water; it is afterwards ground to powder and elutriated. *Cobalt ultramarine* is a fine blue colour prepared by mixing 16 parts of

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* For the preparation and properties of all these salts, see Watts's Dictionary of Chemistry, vol. i. 1051, first Supplement, p. 479, and second Supplement, p. 363. Their rational formulæ are similar to those of the ammoniacal platinum salts (*q.v.*).

freshly precipitated alumina with 2 parts of cobalt phosphate or arsenate: this mixture is dried and slowly heated to redness. By daylight the colour is pure blue, but by artificial light it is violet. A similar compound, of a fine green colour, is formed by igniting zinc oxide with cobalt-salts. *Zaffre* is the roasted cobalt ore mixed with siliceous sand, and reduced to fine powder: it is used in enamel painting. A mixture in due proportions of the oxides of cobalt, manganese, and iron is used for giving a fine black colour to glass.

NICKEL.

Symbol, Ni. Atomic weight, 58·8.

THIS metal, as already observed, is a constant constituent of meteoric iron. It is found in tolerable abundance in some of the metal-bearing veins of the Saxon mountains, in Westphalia, Hesse, Hungary, and Sweden, chiefly as arsenide, the *kupfernickel* of mineralogists, so called from its yellowish-red colour. The word *nickel* is a term of detraction, having been applied by the old German miners to what was looked upon as a kind of false copper ore. The artificial, or perhaps merely fused product, called *speiss*, has nearly the same composition.

From either of these substances a pure salt of nickel may be obtained in the manner already described in connection with cobalt-salts (p. 493). The cobalt having been thrown down by Rose's process, as sesquioxide, the nickel remains in solution, and may be precipitated as hydroxide by potash, after the barium also contained in the solution has been thrown down by sulphuric acid.

Metallic nickel is easily prepared by exposing the oxalate to a high white heat, in a crucible lined with charcoal, or by reducing one of the oxides by means of hydrogen at a high temperature. It is a white, malleable metal, having a density of 8·8, a high melting point, and a less degree of oxidability than iron, since it is but little attacked by dilute acids. Nickel is strongly magnetic, but loses this property when heated to 350°.

Nickel Chloride, $NiCl_2$, is easily prepared by dissolving oxide or carbonate of nickel in hydrochloric acid. A green solution is obtained, which furnishes crystals of the same colour containing water. When rendered anhydrous by heat, the chloride is yellow, unless it contains cobalt, in which case it has a tint of green.

Nickel Oxides and **Oxysalts.**—Nickel forms two oxides analogous to the two principal oxides of iron.

The *monoxide*, NiO, is prepared by heating the nitrate to redness, or by precipitating a soluble nickel salt with caustic potash, and

washing, drying, and igniting the apple-green hydroxide thrown down. It is an ashy-grey powder, freely soluble in acids, which it completely neutralises, forming salts isomorphous with those of magnesium and the other members of the same group. Nickel salts, when hydrated, have usually a beautiful emerald-green colour; in the anhydrous state they are yellow.

The *sesquioxide*, Ni_2O_3, is a black insoluble substance, prepared by passing chlorine through the hydroxide suspended in water; nickel chloride is then formed, and the oxygen of the oxide decomposed is transferred to a second portion. It is also produced when a salt of nickel is mixed with a solution of bleaching-powder. The sesquioxide is decomposed by heat, and evolves chlorine when treated with hot hydrochloric acid.

Nickel Sulphate, $NiSO_4,7H_2O$.—This is the most important of the nickel salts. It forms green prismatic crystals, which require 3 parts of cold water for solution. Crystals with 6 molecules of water have also been obtained. It forms with the sulphates of potassium and ammonium beautiful double salts, $NiK_2(SO_4)_2,6H_2O$, and $Ni(NH_4)_2(SO_4)_2,6H_2O$, isomorphous with the corresponding magnesium salts.

When a strong solution of oxalic acid is mixed with sulphate of nickel, a pale bluish-green precipitate of oxalate falls after some time, very little nickel remaining in solution. The oxalate can thus be obtained for preparing the metal.

Nickel Carbonate, $NiCO_3$.—When solutions of nickel sulphate or chloride and of sodium carbonate are mixed, a pale-green precipitate falls, which is a combination of nickel carbonate and hydroxide. It is readily decomposed by heat.

Nickel-salts are well characterised by their behaviour with reagents.

Caustic alkalis give a pale apple-green precipitate of hydroxide, insoluble in excess. *Ammonia* affords a similar precipitate, which is soluble in excess, with deep purplish-blue colour. *Potassium* and *sodium carbonates* give pale-green precipitates. *Ammonium carbonate*, a similar precipitate, soluble in excess, with blue colour. *Potassium ferrocyanide* gives a greenish-white precipitate. *Potassium cyanide* produces a green precipitate, which dissolves in an excess of the precipitant to an amber-coloured liquid, and is reprecipitated by addition of hydrochloric acid. *Hydrogen sulphide* occasions no change, if the nickel be in combination with a strong acid. *Ammonium sulphide* produces a black precipitate of nickel sulphide, which dissolves slightly in excess of the precipitant, with dark-brown colour. Nickel sulphide when once precipitated, is insoluble in dilute hydrochloric acid; it is soluble in nitromuriatic and in hot nitric acid.

Nickel is used for the preparation of a white alloy, sometimes called German silver, made by melting together 100 parts of copper, 16 of zinc, and 40 of nickel. This alloy is very malleable, and takes a high polish.

Alloys of copper with nickel and zinc, or with nickel alone, are also used in Germany, Belgium, Switzerland, and the United States, for the manufacture of small coin. The advantages of nickel coining are that, nickel being dearer than copper, the coins can be made smaller for the same value; that the alloy is hard and therefore wears well; and further, that its manufacture requires experienced workmen and the use of powerful machinery.

Another application, of recent introduction, is the electrolytic deposition of nickel on iron, steel, copper, brass, and other metals, from a solution of nickel sulphate or the double sulphate or chloride of nickel and ammonium, or nickel and potassium. The nickel is deposited in dense layers, capable of receiving a good polish.

METALS OF THE CHROMIUM GROUP.

Chromium.	Tungsten.
Molybdenum.	Uranium.

These metals are hexads, their highest oxides, which are of acid character, having the composition MO_3; they also form lower oxides, MO_2, M_2O_3, M_3O_4, and MO, more or less basic, and analogous in composition to the basic oxides of manganese, iron, cobalt, and nickel. Chromium, molybdenum, and tungsten form hexfluorides analogous to the highest oxides, and uranium forms an oxychloride, UO_2Cl_2, also of analogous composition.

CHROMIUM.

Symbol, Cr. Atomic weight, 52·4.

Chromium is found in the state of oxide, in combination with iron oxide, somewhat abundantly in the Shetland Islands, and elsewhere; as lead chromate it constitutes a very beautiful mineral, from which it was first obtained. The metal itself is prepared in a half-fused condition by mixing the oxide with half its weight of charcoal powder, enclosing the mixture in a crucible lined with charcoal, and then subjecting it to the very highest heat of a powerful furnace.

acids. The anhydrous sesquioxide may be prepared in a beautifully crystalline form by heating potassium pyrochromate, $K_2O,2CrO_3$, to full redness in an earthen crucible. One-half of the chromium trioxide contained in that salt then suffers decomposition, oxygen being disengaged, and sesquioxide left. The melted mass is treated with water, which dissolves out normal potassium chromate, and the oxide is washed and dried. Chromium sesquioxide communicates a fine green tint to glass, and is used in enamel painting. The crystalline sesquioxide is employed in the manufacture of razor-strops. From a solution of chromium sesquioxide in potash or soda, green gelatinous chromic hydroxide separates on standing. When finely powdered and dried over sulphuric acid, it consists of $Cr_2O_3,6H_2O$ or $Cr_2(HO)_6,3H_2O$. A hydroxide may also be prepared by boiling a somewhat dilute solution of potassium pyrochromate strongly acidulated with hydrochloric acid, with small successive portions of sugar or alcohol. In the former case carbon dioxide escapes: in the latter, aldehyde and acetic acid are formed, and the chromic acid of the salt becomes converted into chromium trichloride, the colour of the liquid changing from red to deep green. The reduction may also be effected, as already observed, by hydrochloric acid alone. A slight excess of ammonia precipitates the hydroxide from its solution. It has a pale purplish-green colour, which becomes full green on ignition; a great shrinking of volume and sudden incandescence are observed when the hydroxide is decomposed by heat.

Chromium sesquioxide is a weak base, resembling iron sesquioxide and alumina, with which it is isomorphous; its salts (chromic salts) have a green or purple colour, and are said to be poisonous.

Chromic sulphate, $Cr_2(SO_4)_3$, is prepared by dissolving the hydroxide in dilute sulphuric acid. It unites with the sulphates of potassium and ammonium, giving rise to magnificent double salts, which crystallise in regular octohedrons of a deep claret-colour, and are analogous in constitution to common alum, the aluminium being replaced by chromium. The ammonium-salt, for example, has the composition $Cr''(NH_4)(SO_4)_2,12H_2O$. The finest crystals are obtained by spontaneous evaporation, the solution being apt to be decomposed by heat.

The *dioxide*, CrO_2, possibly a chromic chromate, CrO_3,Cr_2O_3, is a brown substance obtained by digesting chromic oxide with excess of chromic acid, or by partial reduction of chromic acid with alcohol, sulphurous acid, &c.

Chromium Trioxide, CrO_3; in combination with water, forming *Chromic acid*, $CrO_3,H_2O = H_2CrO_4 = (CrO_2)(OH)_2$. Whenever chromium sesquioxide is strongly heated with an alkali, in contact with air, oxygen is absorbed and the trioxide is generated. Chromium trioxide may be obtained nearly pure, and in a state of great beauty, by mixing 100 measures of a cold saturated solution of potassium pyrochromate with 150 measures of oil of vitriol, leaving the whole to cool, pouring off the mother-liquor, and leaving the

crystals to drain upon a tile, closely covered by a glass or bell-jar. It is also formed by decomposing the hexfluoride with a small quantity of water. Chromium trioxide crystallises in brilliant crimson-red prisms very deliquescent and soluble in water: the solution is instantly reduced by contact with organic matter.

Chromic acid is bibasic and analogous in composition to sulphuric acid; its salts are isomorphous with the corresponding sulphates.

Potassium Chromate, K_2CrO_4 or $(CrO_2)(OK)_2$.—This salt is made directly from the native *chrome-iron ore*, which is a compound of chromium sesquioxide and ferrous oxide, analogous to magnetic iron ore, by calcination with nitre or with potassium carbonate, or with caustic potash, the ore being reduced to powder and heated for a long time with the alkali in a reverberatory furnace. The product, when treated with water, yields a yellow solution, which, on evaporation, deposits anhydrous crystals of the same colour, isomorphous with potassium sulphate. Potassium chromate has a cool, bitter, and disagreeable taste, and dissolves in 2 parts of water at 15·5°.

Potassium Dichromate, or *Pyrochromate*, K_2CrO_4,CrO_3, analogous in composition to the pyrosulphate (p. 367), is obtained by treating the preceding salt with a moderate quantity of sulphuric acid, whereby one-half of the base is removed, and the chromate is converted into pyrochromate. This salt, of which immense quantities are manufactured for use in the arts, crystallises by slow evaporation in beautiful red tabular crystals, derived from a triclinic prism. It melts when heated, and is soluble in 10 parts of water; the solution has an acid reaction.

Potassium Trichromate, $K_2O,3CrO_3$ or $K_2CrO_4,2CrO_3$, may be obtained in crystals by dissolving the dichromate in an aqueous solution of chromic acid, and leaving it to evaporate over sulphuric acid.

Lead Chromate, $PbCrO_4$.—This salt, the *chrome-yellow* of the painter, is obtained, as a brilliant yellow precipitate, on mixing solutions of potassium chromate or pyrochromate with lead nitrate or acetate. On boiling it with lime-water, one-half of the acid is withdrawn, and a basic lead chromate of an orange-red colour left. The basic chromate is also formed by adding lead chromate to fused nitre, and afterwards dissolving out the soluble salts by water: the product is crystalline, and rivals vermilion in beauty of tint. The yellow and orange chrome colours are fixed upon cloth by alternate application of the chromium and lead solutions, and in the latter case by passing the dyed stuff through a bath of boiling lime-water.

Silver Chromate, Ag_2CrO_4, is precipitated as a reddish-brown powder when solutions of potassium chromate and silver nitrate are mixed. It dissolves in hot dilute nitric acid, and separates, on cooling, in small ruby-red platy crystals. The chromates of *barium*, *zinc*, and *mercury* are insoluble; the first two are yellow, the last is brick-red.

Perchromic Acid is obtained, according to Barreswil, by mixing chromic acid with dilute hydrogen dioxide, or potassium pyro-

two isomeric modifications, viz.—1. *Ordinary tungstic acid*, which is insoluble in water, and forms insoluble salts with all metals, except the alkali-metals, and magnesium; 2. *Metatungstic acid*, which is soluble in water, and forms soluble salts with nearly all metals. Ordinary tungstic acid forms normal salts containing M_2WO_4 or M_2O,WO_3, and acid salts containing $3M_2O,7WO_3$, which may perhaps be regarded as double salts composed of diacid and triacid tungstates, that is, as $2(M_2O,2WO_3) + M_2O,3WO_3$. The tungstates of potassium and sodium, especially the latter, are sometimes used as mordants in dyeing, in place of stannates; also for rendering muslin and other light fabrics uninflammable. Tungstous tungstate, WO_2,WO_3, which has the composition of *tungsten pentoxide*, W_2O_5, is a blue substance formed by reducing tungstic oxide or tungstic acid with zinc and hydrochloric acid; also by heating ammonium tungstate to redness in a retort.

Metatungstates.—These salts, which have the composition of quadracid tungstates, $M_2O,4WO_3$, are formed from ordinary tungstates by addition of tungstic acid, or by removing part of the base by means of an acid. They are for the most part soluble and crystallisable. By decomposing barium metatungstate with dilute sulphuric acid, and evaporating the filtrate in a vacuum, hydrated metatungstic acid is obtained in quadratic octohedrons, apparently containing $H_2W_4O_{13},31H_2O$; it is very soluble in water.

*Silicotungstates.**—By boiling gelatinous silica with acid potassium tungstate, a crystalline salt is obtained, having the composition of a diacid potassium tungstate, $6(K_2O,2WO_3)$, or $K_{12}O_6,12WO_3$, in which one-third of the potassium is replaced by silicon, viz., $K_8SiO_6,12WO_3$, so that the silicon here enters as a *basylous* element. The resulting solution yields with mercurous nitrate a precipitate of *mercurous silicotungstate;* this, when decomposed by an equivalent quantity of hydrochloric acid, yields a solution of *hydrogen silicotungstate*, or *silicotungstic acid;* and the other silicotungstates, which are all soluble, are obtained by treating the acid with carbonates.

Silicodecitungstic acid, $H_8SiO_6,10WO_3$, is obtained as an ammonium salt by boiling gelatinous silica with solution of acid ammonium tungstate; and from this, the acid and its other salts may be obtained in the same manner as the preceding. The silicodecitungstates are very unstable, and the acid is decomposed by mere evaporation, depositing silica, and being converted into *tungstosilicic acid*, which is isomeric with silicotungstic acid, and likewise decomposes carbonates. All three of these acids are capable of exchanging either one-half or the whole of their basic hydrogen for metals, thereby forming acid and neutral salts; silicotungstic acid also forms an acid sodium salt in which only one-fourth of the hydrogen is replaced by sodium.

* Marignac, Ann. Chim. Phys. [4], iii. 5; Watts's Dictionary of Chemistry, v. 915.

Tungsten Sulphides.—The *disulphide*, or *Tungstous sulphide*, WS_2, is obtained in soft, black, needle-shaped crystals by igniting tungsten, or one of its oxides, with sulphur.

The *trisulphide*, or *Tungstic sulphide*, WS_3, is formed by dissolving tungstic acid in ammonium sulphide, and precipitating with an acid, or by adding hydrochloric acid to the solution of an alkaline tungstate saturated with hydrogen sulphide. It is a light-brown precipitate, turning black when dry. It unites easily with basic metallic sulphides, forming the *thiotungstates*, M_2WS_4, analogous to the normal tungstates.

Reactions of Tungsten-compounds.—Soluble tungstates, or metatungstates, supersaturated with sulphuric, hydrochloric, phosphoric, oxalic, or acetic acid, yield, on the introduction of a piece of *zinc*, a beautiful blue colour, arising from the formation of blue tungsten oxide. A soluble tungstate, mixed with *ammonium sulphide*, and then with excess of acid, yields a light-brown precipitate of tungstic sulphide soluble in ammonium sulphide. *Hydrogen sulphide* does not precipitate the acidulated solution of a tungstate, but turns it blue, owing to the formation of a blue oxide. Ordinary tungstates give, with *potassium ferrocyanide*, after addition of hydrochloric acid, a brown flocculent precipitate, soluble in pure water free from acid; metatungstates give no precipitates. *Acids*, added to solutions of ordinary tungstates, throw down a white or yellow precipitate of tungstic acid; with metatungstates no precipitate is obtained.

All tungsten compounds form colourless beads with borax and phosphorus salt, in the outer blowpipe flame. With *borax*, in the inner flame, they form a yellow glass, if the quantity of tungsten is somewhat considerable, but colourless with a smaller quantity. With *phosphorus salt* in the inner flame they form a glass of a pure blue colour, unless metallic oxides are present, which modify it; in presence of iron the glass is blood-red, but the addition of metallic tin renders it blue.

Steel, alloyed with a small quantity of tungsten, acquires extraordinary hardness. Wootz, or Indian steel, contains tungsten. Tungsten has also a remarkable effect on steel in increasing its power of retaining magnetism when hardened. A horse-shoe magnet of ordinary steel, weighing two pounds, is considered of good quality when it bears seven times its own weight; but, according to Siemens, a similar magnet made with steel containing tungsten may be made to carry twenty times its weight suspended from the armature.*

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* Journal of the Chemical Society, 1868, vol. xxi, p. 284.

URANIUM.

Symbol, U. Atomic weight, 240.

THIS metal is found in a few minerals, as *pitchblende*, which is an oxide, and *uranite*, which is a phosphate; the former is its principal ore. The metal itself is isolated by decomposing the chloride with potassium or sodium, and is obtained as a black coherent powder, or in fused white malleable globules, according to the manner in which the process is conducted. It is permanent in the air at ordinary temperatures, and does not decompose water; but in the pulverulent state it takes fire at 207°, burning with great splendour and forming a dark-green oxide. It unites also very violently with chlorine and with sulphur.

Uranium forms two classes of compounds: viz., the uranous compounds, in which it is quadrivalent, *e.g.*, UCl_4, UO_2, $U(SO_4)_2$, &c., and the uranic compounds, in which it is sexvalent, *e.g.*,

$$UO_3,\ UO_2Cl_2,\ UO_2(NO_3)_2,\ UO_2(SO_4).$$

There are also two oxides intermediate between uranous and uranic oxide. There is no chloride, bromide, iodide, or fluoride corresponding with uranic oxide, such as UCl_6: neither are there any normal uranic oxysalts, such as $U(NO_3)_6$, $U(SO_4)_3$, &c.; but all the uranic salts contain the group UO_2, which may be regarded as a bivalent radicle (uranyl), uniting with acids in the usual proportions, and forming normal salts; thus—

Uranic oxide or Uranyl oxide . .	$(UO_2)O$
Uranic oxychloride or Uranyl chloride .	$(UO_2)Cl_2$
Uranic nitrate or Uranyl nitrate . .	$(UO_2)(NO_3)_2$
Uranic sulphate or Uranyl sulphate .	$(UO_2)(SO_4)$.

This view of the composition of the uranic salts is not, however, essential, since they may also be formulated as basic salts in the manner above illustrated.

Chlorides.—*Uranous chloride*, UCl_4, is formed, with vivid incandescence, by burning metallic uranium in chlorine gas, also by igniting uranous oxide in hydrochloric acid gas, and, lastly, by heating uranoso-uranic oxide with charcoal in a current of chlorine. It crystallises in dark-green regular octohedrons, and dissolves easily in water, forming an emerald-green solution, which is decomposed when dropped into boiling water, giving off hydrochloric acid, and yielding a brown precipitate of hydrated uranous oxide. It is a powerful deoxidising agent, reducing gold and silver, converting ferric salts into ferrous salts, &c. Its vapour-density, determined in V. Meyer's apparatus (p. 70) was found to be 13·33 (hydrogen = 1),

which agrees closely with the theoretical number 13·21 deduced from the atomic weight of uranium, 240.*

Uranic oxychloride, or *Uranyl chloride*, UO_2Cl_2, is formed when dry chlorine gas is passed over red-hot uranous oxide, as an orange-yellow vapour, which solidifies to a yellow crystalline fusible mass, easily soluble in water. It forms double salts with the chlorides of the alkali-metals,—the potassium salt, for example, having the composition $UO_2Cl_2,2KCl,2H_2O$.

Uranous Bromide, UBr_4, is prepared by heating a mixture of uranoso-uranic oxide and charcoal in a current of carbon dioxide laden with bromine-vapour, and collects on the cooler parts of the tube in black glistening leaflets, which are converted by heat into a brown vapour, and may be sublimed unchanged. It is extremely hygroscopic. Vapour-density, by experiment 19·46, by calculation, 19·36 (Zimmermann).

Fluorides.—Uranoso-uranic oxide, U_3O_8, treated with aqueous hydrofluoric acid, yields a bulky green powder consisting of uranous fluoride, UF_4, and a yellow solution which, on evaporation, leaves uranic oxyfluoride or uranyl fluoride, UO_2F_2. When uranous fluoride is heated in a closed crucible, a white sublimate is formed, and if the crucible be then left to cool, and this sublimate be removed, a fresh white sublimate will be formed, and so on till nothing is left in the crucible but uranous oxide, UO_2. The white sublimate, for the formation of which access of air is of course necessary, is isomeric with the yellow oxyfluoride above mentioned, and is distinguished as α-UO_2F_2.†

Oxides.—*Uranous oxide*, UO_2, formerly mistaken for metallic uranium, is obtained by heating the oxide, U_3O_8, or uranic oxalate, in a current of hydrogen. It is a brown powder, sometimes highly crystalline. In the finely divided state it is pyrophoric. It dissolves in acids, forming green salts.

Uranoso-uranic oxide, $U_3O_8 = UO_2,2UO_3$.—This oxide forms the chief constituent of pitchblende. It is obtained artificially by igniting the metal or uranous oxide in contact with the air, or by gentle ignition of uranic oxide or uranic nitrate. It forms a dark-green velvety powder, of specific gravity 7·1 to 7·3. When ignited in hydrogen, or with sodium, charcoal, or sulphur, it is reduced to uranous oxide. When ignited alone, it yields a black oxide, U_2O_5. Uranoso-uranic oxide dissolves in strong sulphuric or hydrochloric acid, yielding a mixture of uranous and uranic salt; by nitric acid it is oxidised to uranic nitrate.

Uranic oxide, or *Uranyl oxide*, UO_3.—Uranium and its lower oxides dissolve in nitric acid, forming uranic nitrate; and when this

* Zimmermann, Berichte der deutschen chemischen Gesellschaft, xiv. 1934.

† A. Smithells, Chem. Soc. Journal, xliii. 125.

interior. The use of tin solutions in dyeing and calico-printing has been already mentioned.

TITANIUM.

Symbol, Ti. Atomic weight, 48.

This is one of the rarer metals, and is never found in the metallic state. The most important titanium minerals are *rutile*, *brookite*, and *anatase*, which are different forms of titanic oxide, and the several varieties of *titaniferous iron*, consisting of ferrous titanate, sometimes alone, but more generally mixed with ferric or ferroso-ferric oxide. Occasionally in the slag adhering to the bottom of blast-furnaces in which iron ore is reduced, small brilliant copper-coloured cubes are found, hard enough to scratch glass, and in the highest degree infusible. This substance, of which a single smelting furnace in the Hartz produced as much as 80 pounds, was formerly believed to be metallic titanium. Wöhler, however, has shown it to be a compound of titanium cyanide with titanium nitride. When these crystals are powdered, mixed with potassium hydroxide, and fused, ammonia is evolved, and potassium titanate is formed.

Metallic titanium in a finely divided state may be obtained by heating titanium and potassium fluoride with potassium. This element is remarkable for its affinity for nitrogen: when heated in the air, it simultaneously absorbs oxygen and nitrogen.

Titanium is tetradic, like tin, and forms two classes of compounds: the titanic compounds, in which it is quadrivalent, *e.g.*, $TiCl_4$, TiO_2, and the titanous compounds, in which it is apparently trivalent, but really also quadrivalent, *e.g.*, Ti_2Cl_6, or $Cl_3Ti.TiCl_3$.

Chlorides.—*Titanous chloride*, Ti_2Cl_6, is produced by passing the vapour of titanic chloride mixed with hydrogen through a red-hot tube; it forms dark violet scales having a strong lustre. *Titanic chloride*, $TiCl_4$, is prepared by passing chlorine over an ignited mixture of titanic oxide and charcoal. It is a colourless, volatile, fuming liquid, having a specific gravity of 1·7609 at 0°, vapour-density = 6·836, and boiling at 135°. It unites very violently with water, and forms definite compounds with ammonia, ammonium chloride, hydrogen cyanide, cyanogen chloride, phosphine, and sulphur tetrachloride.

Fluorides.—*Titanous fluoride*, Ti_2F_6, is obtained as a violet powder by igniting potassio-titanic fluoride in hydrogen gas, and treating the resulting mass with hot water. *Titanic fluoride*, TiF_4, passes over as a fuming colourless liquid, when titanic oxide is distilled with fluor-spar and fuming sulphuric acid in a platinum apparatus. It unites with hydrofluoric acid and metallic fluorides,

forming double salts called titano-fluorides or fluotitanates, isomorphous with the silicofluorides, zircofluorides, &c., *e.g.*, $TiF_4,2KF$; TiF_4,CaF_2.

Oxides.—The *sesquioxide*, or *Titanous oxide*, Ti_2O_3, is obtained by igniting the dioxide in hydrogen, as a black powder, which, when heated in the air to a very high temperature, oxidises to titanic oxide.

The *dioxide*, or *Titanic oxide*, occurs native in three different forms, viz., as rutile and anatase, which are dimetric, and brookite, which is trimetric ; of these anatase is the purest, and rutile the most abundant. To obtain pure titanic oxide, rutile or titaniferous iron ore, reduced to fine powder, is fused with twice its weight of potassium carbonate, and the fused mass is dissolved in dilute hydrofluoric acid, whereupon titano-fluoride of potassium soon begins to separate. From the hot aqueous solution of this salt, ammonia throws down snow-white ammonium titanate, which is easily soluble in hydrochloric acid, and when ignited gives reddish-brown lumps of titanic oxide. This oxide is insoluble in water, and in all acids except strong sulphuric acid. By fusing it with six times its weight of acid potassium sulphate, a clear yellow mass is obtained, which dissolves perfectly in warm water.

Titanic oxide appears to form two hydroxides or acids, analogous to stannic and metastannic acids. One of these, called titanic acid, is precipitated by ammonia from a solution of titanic chloride, as a white powder which dissolves easily in sulphuric, nitric, and hydrochloric acids, even when these acids are rather dilute ; but these dilute solutions, when boiled, deposit metatitanic hydrate as a soft white powder, which, like the anhydrous oxide, is insoluble in all acids except strong sulphuric acid.

The titanates have not been much studied ; most of them may be represented by the formulæ $M_4TiO_4 = 2M_2O,TiO_2$, and $M_2TiO_3 = M_2O,TiO_2$ (the symbol M denoting a univalent metal). The titanates of calcium and iron occur as natural minerals. The titanates of the alkali-metals are formed by fusing titanic oxide with alkaline hydroxides, carbonates, or acid sulphates—some of them also in the wet way. When finely pulverised and levigated, they dissolve in moderately warm, concentrated hydrochloric acid ; but the greater part of the dissolved titanic acid is precipitated on boiling the solution with dilute acid. The normal titanates of the alkali-metals, M_2TiO_3, are insoluble in water, but soluble in acids. The titanates of the earth-metals and heavy metals are insoluble, and may be obtained by precipitation.

In a solution of titanic acid in hydrochloric acid, containing as little free acid as possible, *tincture of galls* produces an orange-coloured precipitate ; *potassium ferrocyanide*, a dark brown precipitate.

Titanic oxide fused with borax, or better with microcosmic salt in the inner blow-pipe flame, forms a glass which is yellow while hot,

but becomes violet on cooling. The delicacy of this reaction is much increased by melting a little metallic zinc in the bead.

ZIRCONIUM.

Symbol, Zr. Atomic weight, 90.

This is a tetrad metal, intermediate in many of its properties between aluminium and silicon. Its oxide, zirconia, was first obtained by Klaproth, in 1789, from zircon, which is a silicate of zirconium. It has since been found in fergusonite, eudialyte, and two or three other rare minerals.

Zirconium, like silicon, is capable of existing in three different states, amorphous, crystalline, and graphitoïdal.* The amorphous and crystalline varieties are obtained by processes similar to those described for preparing the corresponding modifications of silicon (p. 247); graphitoïdal zirconium was once obtained, by Troost, in attempting to decompose sodium zirconate with iron, in light scales of a steel-grey colour. Amorphous zirconium when heated in the air takes fire at a heat somewhat below redness, and burns with a bright light forming zirconia. Crystalline zirconium forms very hard brittle scales resembling antimony in colour and lustre; it burns in the air only at the heat of the oxy-hydrogen blow-pipe, but takes fire at a red heat in chlorine gas. Zirconium is but little attacked by the ordinary acids; but hydrofluoric acid dissolves it readily, with evolution of hydrogen.

Zirconium Oxide, or **Zirconia**, ZrO_2, is prepared by strongly igniting zircon (zirconium silicate), with four times its weight of dry sodium carbonate and a small quantity of sodium hydrate. The silica is separated from the fused mass by hydrochloric acid, as described in the case of beryllia; the resulting solution is treated with ammonia, which throws down zirconia generally mixed with ferric oxide; the precipitate is redissolved in hydrochloric acid; and the solution is boiled with excess of sodium thiosulphate as long as sulphurous acid continues to escape, whereby pure zirconia is precipitated, the whole of the iron remaining in the solution. Zirconia thus obtained forms a white powder, or hard lumps, of specific gravity 4·35 to 4·9. By fusing it with borax in a pottery furnace and dissolving out the soluble salts with hydrochloric acid, zirconia is obtained in small quadratic prisms isomorphous with the native oxides of tin and titanium.

Zirconium hydroxides are obtained by precipitating the solution of a zirconium salt with ammonia: the precipitate contains $ZrH_2O_3 = ZrO_2,H_2O$, or $ZrH_4O_4 = ZrO_2,2H_2O$, according to the temperature at which it is dried.

* Troost, Bull. Soc. Chim., 1866, i. 213.

Zirconia acts both as a base and as an acid. After ignition it is insoluble in all acids except hydrofluoric and very strong sulphuric acid, but the hydroxide dissolves easily in acids, forming the zirconium salts; the normal sulphate has the composition $Zr(SO_4)_2$, or $ZrO_2,2SO_3$.

Compounds of zirconia with the stronger bases, called zirconates, are obtained by precipitating a zirconium salt with potash or soda, or by igniting zirconia with an alkaline hydrate. *Potassium zirconate* dissolves completely in water. Three *sodium zirconates* have been formed, containing $Na_2ZrO_3 = Na_2O,ZrO_2$; $Na_4ZrO_4 = 2Na_2O,ZrO_2$; and $Na_2Zr_8O_{17} = Na_2O,8ZrO_2$.

Zirconium Fluoride, ZrF_4, is obtained by dissolving zirconia, or the hydroxide, in hydrofluoric acid; or in the anhydrous state, by igniting zirconia with ammonium and hydrogen fluoride till all the ammonium fluoride is driven off. It unites with other metallic fluorides, forming double salts, called zircofluorides or fluozirconates, which are isomorphous with the corresponding silicofluorides, stannofluorides, and titanofluorides, and are mostly represented by the formulæ—

$$4MF,ZrF_4;\ 3MF,ZrF_4;\ 2MF,ZrF_4;\ MF,ZrF_4,$$

in which M denotes a monad metal. The sodium salt, however, has the composition $5NaF,3ZrF_4$.

THORIUM.

Symbol, Th. Atomic weight, 231·5.

This very rare metal was discovered in 1828 by Berzelius, in thorite, a mineral from the Norwegian island Lovön, in which it exists as a silicate. It has since been found in euxenite, pyrochlore, and a few other minerals, all very scarce.

Metallic thorium is obtained by reducing the chloride with potassium or sodium, as a grey powder, which acquires metallic lustre by pressure, and has a density of 7·66 to 7·795. It is not oxidised by water, dissolves easily in nitric, slowly in hydrochloric acid, and is not attacked by caustic alkalis.

Thorium forms but one class of compounds, in all of which it is quadrivalent.

Thorium Oxide, or **Thoria**, ThO_2, is prepared by decomposing thorite with hydrochloric acid, separating the silica in the usual way, treating the filtered solution with hydrogen sulphide to separate lead and tin, and precipitating the thoria by ammonia, together with small quantities of the oxides of iron, manganese, and uranium. To get rid of these, the precipitate is redissolved in hydrochloric acid,

and the hot saturated solution is boiled with a solution of normal potassium sulphate. The thorium is thereby precipitated as thorium and potassium sulphate; and from the solution of this salt in hot water, the thorium is precipitated by alkalis as a hydroxide, which, on ignition, yields pure thoria.

Thoria is white, and very heavy, its specific gravity being 9·402. After ignition it is insoluble in nitric and hydrochloric acids, and dissolves in strong sulphuric acid only after prolonged heating. The *hydroxide*, precipitated from thorium salts by alkalis, dissolves easily in acids.

Thorium Chloride, $ThCl_4$, prepared by igniting an intimate mixture of thoria and charcoal in chlorine gas, sublimes in white shining crystals. It forms double salts with the chlorides of the alkali-metals.

Thorium Sulphate, $Th(SO_4)_2$, crystallises with various quantities of water, according to the temperature at which its solution is evaporated. *Thorium and potassium sulphate*, $ThK_4(SO_4)_4.2H_2O$, separates as a crystalline powder when a crust of potassium sulphate is suspended in a solution of thorium sulphate. It is easily soluble in water, but insoluble in alcohol and in solution of potassium sulphate.

METALS OF THE ANTIMONY GROUP.

Vanadium.	Tantalum.
Antimony.	Niobium.
Bismuth.	

VANADIUM.

Symbol, V. Atomic weight, 51·2.

VANADIUM is found, in small quantity, in some iron ores, also as *vanadate of lead*. It has likewise been discovered in the iron slag of Staffordshire, and more recently, by Roscoe,* in larger quantity in the copper-bearing beds at Alderley Edge and Mottram St. Andrews, in Cheshire.

Metallic vanadium is obtained by prolonged ignition of the dichloride in pure dry hydrogen, as a greyish-white powder, appearing under the microscope as a crystalline mass, with a strong silver-white lustre. It is non-volatile; decomposes water at 100°; does not tarnish in the air; burns with brilliant scintillations when thrown into a flame; burns vividly when quickly heated in oxygen, forming

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* Proceedings of the Royal Society, xvi. 223.

the pentoxide; is insoluble in hydrochloric acid; dissolves slowly in hydrofluoric acid with evolution of hydrogen, rapidly in nitric acid, forming a blue solution. In a current of chlorine it takes fire, and is converted into the tetrachloride.

Vanadium was, till lately, regarded as a hexad metal, analogous to tungsten and molybdenum; but Roscoe has shown that it is a pentad, belonging to the phosphorus and arsenic group. This conclusion is based upon the composition of the oxides and oxychlorides; and on the isomorphism of the vanadates with the phosphates.

Vanadium Oxides.—Vanadium forms five oxides, represented by the formulæ, V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5, analogous, therefore, to the oxides of nitrogen.

The *monoxide*, V_2O, is formed by prolonged exposure of metallic vanadium to the air at ordinary temperature, more quickly at a dull red heat. It is a brown substance, which, when heated in the air, is gradually converted into the higher oxides.

The *dioxide*, V_2O_2, which was regarded by Berzelius as metallic vanadium, is obtained by reducing either of the higher oxides with potassium, or by passing the vapour of vanadium oxytrichloride, ($VOCl_3$), mixed with excess of hydrogen, through a combustion tube containing red-hot charcoal. As obtained by the second process, it forms a light-grey glittering powder, or a metallically lustrous crystalline crust, having a specific gravity of 3·64, brittle, very difficult to fuse, and a conductor of electricity. When heated to redness in the air, it takes fire and burns to black oxide. It is insoluble in sulphuric, hydrochloric, and hydrofluoric acid, but dissolves easily in nitromuriatic acid, forming a dark-blue liquid.

The dioxide may be prepared in solution by the action of nascent hydrogen (evolved by metallic zinc, cadmium, or sodium-amalgam), on a solution of vanadic acid in sulphuric acid. After passing through all shades of blue and green, the liquid acquires a permanent lavender tint, and then contains the vanadium in solution as dioxide, or as hypovanadious salt. This compound absorbs oxygen more rapidly than any other known substance, and bleaches indigo and other vegetable colours as quickly as chlorine.

Vanadium dioxide may be regarded as entering into many vanadium compounds, as a bivalent radicle (just like uranyl in the uranic compounds), and may therefore be called *vanadyl*.

Vanadium trioxide, V_2O_3, or *Vanadyl monoxide*, $(V_2O_2)''O$, is obtained by igniting the pentoxide in hydrogen gas, or in a crucible lined with charcoal. It is a black powder, with an almost metallic lustre, and infusible; by pressure it may be united into a coherent mass which conducts electricity. When exposed warm to the air, it glows, absorbs oxygen, and is converted into pentoxide. At ordinary temperatures, it slowly absorbs oxygen, and is converted into tetroxide. By ignition in chlorine gas it is converted into vanadyl trichloride and vanadium pentoxide. It is insoluble in acids, but may be obtained in solution by the reducing action of nascent

Lead metavanadate occurs native as *dechenite;* the orthovanadate also, combined with lead chloride, as *vanadinite* or *vanadite*, $PbCl_2,3Pb_3(VO_4)_2$, the mineral in which vanadium was first discovered. *Descloizite* is a diplumbic vanadate, $Pb_2V_2O_7$, or $2PbO,V_2O_5$, analogous in composition to a pyrophosphate.

The metavanadates are mostly yellow; some of them, however, especially those of the alkaline earth-metals, and of zinc, cadmium, and lead, are converted by warming—either in the solid state, or under water, or in aqueous solution, especially in presence of a free alkali or alkaline carbonate—into isomeric colourless salts. The same transformation takes place also, though more slowly, at ordinary temperatures. The metavanadates of alkali-metal are colourless. The acid vanadates are yellow, or yellowish-red, both in the solid state and in solution: hence the solution of a neutral vanadate becomes yellowish-red on addition of an acid. The metavanadates of ammonium, the alkali-metals, barium, and lead, are but sparingly soluble in water; the other metavanadates are more soluble. The alkaline vanadates are more soluble in pure water than in water containing free alkali or salt: hence they are precipitated from their solutions by addition of alkali in excess, or of salts. The vanadates are insoluble in alcohol. The aqueous solutions of vanadates form yellow precipitates with *antimony*, *copper*, *lead*, and *mercury* salts; with *tincture of galls* they form a deep black liquid, which has been proposed for use as vanadium ink.

Hydrogen sulphide reduces them to hypovanadates, changing the colour from red or yellow to blue, and forming a precipitate of sulphur.

Ammonium sulphide colours the solutions brown-red, and, on adding an acid, a light-brown precipitate is formed, consisting of vanadic sulphide mixed with sulphur, the liquid at the same time turning blue. *Hydrochloric acid* decomposes the vanadates, with evolution of chlorine and formation of vanadium tetroxide.

Vanadium Chlorides.—Three of these compounds have been obtained, viz.: VCl_2, VCl_3, and VCl_4.

The *tetrachloride*, VCl_4, is formed when metallic vanadium or the mononitride is heated in a current of chlorine, or when the vapour of the oxytrichloride, $VOCl_3$, mixed with chlorine, is passed several times over red-hot charcoal. It is a dark yellowish-brown liquid, having a specific gravity of 1·8384 at 0°, boiling at 154°, not solidifying at 18°. Its vapour-density referred to hydrogen is 96·6, which is half the molecular weight $\left(=\frac{51{\cdot}5 + 4 \times 35{\cdot}4}{2}\right)$, showing that the molecule VCl_4 exhibits the normal condensation to 2 volumes of vapour. The tetrachloride is quickly decomposed by water, forming a blue solution of vanadious acid. It does not take up bromine or an additional quantity of chlorine when heated therewith in sealed tubes: hence it appears that vanadium does not readily form pentad compounds with the monatomic chlorous elements.

The *trichloride*, VCl_3, is obtained by decomposition of the tetrachloride, slowly at ordinary temperatures, quickly at the boiling heat; also by warming the trisulphide in a current of chlorine. It crystallises in peach-blossom-coloured shining plates resembling chromic chloride. It is slowly decomposed by water, forming a green solution of hypovanadic acid.

The *dichloride*, VCl_2, obtained by passing the vapour of the tetrachloride mixed with hydrogen through a red-hot tube, crystallises in green micaceous plates, which are decomposed by water, forming a violet solution of hypovanadious acid.

Vanadium Oxychlorides, or Vanadyl Chlorides.—Four of these compounds are known, viz.: $VOCl_3$, $VOCl_2$, VOCl, and V_2O_2Cl.

The *oxytrichloride*, $VOCl_3$ (formerly regarded as vanadium trichloride), is prepared:

(1) By the action of chlorine on the trioxide:

$$3V_2O_3 + Cl_{12} = V_2O_5 + 4VOCl_3.$$

(2) By burning the dioxide in chlorine gas, or by passing that gas over an ignited mixture of the trioxide, tetroxide, or pentoxide, and condensing the vapours in a cooled U-tube.

Vanadium oxytrichloride, or vanadyl trichloride, is a golden-yellow liquid, of specific gravity 1·841 at 14·5°. Boiling-point, 127°. Vapour-density, by experiment, 6·108; by calculation, 6·119. When exposed to the air, it emits cinnabar-coloured vapours, being resolved by the moisture of the air into hydrochloric and vanadic acids. It oxidises magnesium and sodium. Its vapour, passed over perfectly pure carbon at a red heat, yields carbon dioxide; and when passed, together with hydrogen, through a red-hot tube, it yields vanadium trioxide. These reactions show that the compound contains oxygen.

The other oxychlorides of vanadium are solid bodies obtained by partial reduction of the oxytrichloride with zinc or hydrogen.

The second, $VOCl_2$ or $V_2O_2Cl_4$ (hypovanadic chloride), is also produced by dissolving the pentoxide, with aid of heat, in hydrochloric acid, and reducing the green solution with sulphurous acid. The resulting blue liquid leaves, on evaporation over the water-bath, a brown deliquescent residue which yields a blue solution with water (Crow).

The *tribromide*, VBr_3, and the *oxybromides*, $VOBr_3$, and $VOBr_2$, have also been obtained. The first is a greyish-black amorphous solid: the second a dark-red liquid; the third a yellowish-brown deliquescent solid.

Vanadium Sulphides.—Two of these compounds are known, analogous to the tetroxide and pentoxide: both are sulphur-acids. The *tetrasulphide*, or *Vanadious sulphide*, V_2S_4, is a black substance formed by heating the tetroxide to redness in a stream of hydrogen sulphide; also as a hydrate by dissolving a vanadious salt in excess

Sulphides.—The *trisulphide*, or *Antimonious sulphide*, Sb_2S_3, occurs native as a lead-grey, brittle substance, having a radiated crystalline texture, and easily fusible. It may be prepared artificially by melting together antimony and sulphur. When a solution of tartar-emetic is precipitated by hydrogen sulphide, a brick-red precipitate falls, which is the same substance combined with a little water. If the precipitate be dried and gently heated, the water may be expelled without other change of colour than a little darkening, but at a higher temperature it assumes the colour and aspect of the native sulphide. This remarkable change probably indicates a passage from the amorphous to the crystalline state. When powdered antimonious sulphide is boiled in a solution of caustic potash, it is dissolved, antimonious oxide and potassium sulphide being produced; and the latter unites with an additional quantity of antimonious sulphide to form a soluble sulphur-salt, in which the potassium sulphide is the sulphur-base, and the antimonious sulphide is the sulphur-acid:

$$3K_2O + 2Sb_2S_3 = Sb_2O_3 + 3K_2S,Sb_2S_3.$$

The antimonious oxide separates in small crystals from the boiling solution when the latter is concentrated, and the sulphur-salt dissolves an extra portion of antimonious sulphide, which it again deposits on cooling as a red amorphous powder, containing a small admixture of antimonious oxide and potassium sulphide. This is the *kermes mineral* of the old chemists. The filtered solution mixed with an acid gives a potassium salt, hydrogen sulphide, and precipitated antimonious sulphide. Kermes may also be made by fusing a mixture of 5 parts antimonious sulphide and 3 of dry sodium carbonate, boiling the mass in 80 parts of water, and filtering while hot: the compound separates on cooling. The compounds of antimonious sulphide with basic sulphides are called *thio-antimonites;* many of them occur as natural minerals. For example: zinkenite, PbS,Sb_2S_3; feather-ore, $2PbS,Sb_2S_3$; boulangerite, $3PbS,Sb_2S_3$; fahlore, or tetrahedrite, $4Cu_2S,Sb_2S_3$, the antimony being more or less replaced by arsenic, and the copper by silver, iron, zinc, and mercury.

The *pentasulphide*, or *Antimonic sulphide*, Sb_2S_5, formerly called *sulphur auratum*, is also a sulphur-acid, forming salts called *thio-antimonates*, most of which have the composition $3M_2S,Sb_2S_5$ or M_3SbS_4, analogous to the normal orthophosphates and arsenates. When 18 parts of finely powdered antimonious sulphide, 17 parts dry sodium carbonate, 13 parts slaked lime, and 3½ parts sulphur, are boiled in water for some hours, calcium carbonate, sodium antimonate, antimony pentasulphide, and sodium sulphide are produced. The first is insoluble, and the second partially so: the two last-named bodies, on the contrary, unite to form soluble sodium thioantimonate, Na_3SbS_4, which may be obtained by evaporation in beautiful crystals. A solution of this substance, mixed with dilute sulphuric acid, furnishes sodium sulphate, hydrogen sulphide, and

antimony pentasulphide, which falls as a golden-yellow flocculent precipitate.

The thioantimonates of the alkali-metals and alkaline earth-metals are very soluble in water, and crystallise for the most part with several molecules of water. Those of the heavy metals are insoluble, and are obtained by precipitation.

The few salts of antimony soluble in water are distinctly characterised by the orange or brick-red precipitate with *hydrogen sulphide*, which is soluble in a solution of ammonium sulphide, and again precipitated by an acid.

Antimonious chloride, as already observed, is decomposed by *water*, yielding a precipitate of oxychloride. The precipitate dissolves in hydrochloric acid, and the resulting solution gives, with *potash*, a white precipitate of trioxide, soluble in a large excess of the reagent; with *ammonia* the same, insoluble in excess; with *potassium* or *sodium carbonate*, also a precipitate of trioxide, which dissolves in excess, especially of the potassium salt, but reappears after a while. If, however, the solution contains *tartaric acid*, the precipitate formed by potash dissolves easily in excess of the alkali; ammonia forms but a slight precipitate, and the precipitates formed by alkaline carbonates are insoluble in excess. The last mentioned characters are likewise exhibited by a solution of tartar-emetic (potassio-antimonious tartrate). *Zinc* and *iron* precipitate antimony from its solutions as a black powder. *Copper* precipitates it as a shining metallic film, which may be dissolved off by potassium permanganate, yielding a solution which will give the characteristic red precipitate with hydrogen sulphide.

Solid antimony-compounds, fused upon charcoal with sodium carbonate or potassium cyanide, yield a brittle globule of antimony, a thick white fume being at the same time given off, and the charcoal covered to some distance around with a white deposit of oxide.

Besides its application to medicine, antimony is of great importance in the arts, inasmuch as, in combination with lead, it forms *type-metal*. This alloy expands at the moment of solidifying and takes an exceedingly sharp impression of the mould. It is remarkable that both its constituents shrink under similar circumstances, and make very bad castings.

Britannia metal is an alloy of 9 parts tin and 1 part antimony, frequently also containing small quantities of copper, zinc, or bismuth. An alloy of 12 parts tin, 1 part antimony, and a small quantity of copper, forms a superior kind of pewter. Alloys of antimony with tin, or tin and lead, are now much used for machinery-bearings in place of gun-metal. Alloys of antimony with nickel and with silver occur as natural minerals.

Antimony trisulphide enters into the composition of the blue or Bengal lights used at sea, which contain dry nitre 6 parts, sulphur 2 parts, antimony trisulphide 1 part; all in fine powder and intimately mixed.

BISMUTH.

Symbol, Bi. Atomic weight, 210.

Bismuth is found chiefly in the metallic state disseminated through various rocks, from which it may be separated by simple fusion. It occurs as the trioxide or *bismuth ochre*, Bi_2O_3, less frequently as *bismuthite*, Bi_2S_3, and still more sparingly in a few other minerals, as *tetradymite* or *telluric bismuth*, Bi_2Te_3, *eulytin* or bismuth silicate, $Bi(SiO_4)_3$, &c.

Extraction.—The chief sources of bismuth are the Saxon smalt-works, where ores containing bismuth and cobalt are worked. Formerly the bismuth was extracted by simply heating these ores in sloping tubes; but in this way only the portion existing in the metallic state was obtained, and not the whole even of that. The residue was used in the preparation of smalt, and the bismuth again extracted from the cobalt-speiss. At present, however, all bismuth ores are roasted, and afterwards smelted in the pots of the smalt furnaces, with addition of iron, carbon and slag. Two layers are thus obtained, the lower consisting of nearly pure bismuth, which, owing to its low melting point, can be drawn off in the liquid state after the upper layer of cobalt-speiss has solidified. The crude bismuth thus obtained contains only small traces of iron, cobalt, lead, and a few other metals, from which it may be purified by heating it on a slightly inclined iron plate placed over a fire, so that the metal melts and runs down.* A considerable quantity of bismuth from various parts of the world is now worked up in England at the Magnesium Works at Patricroft.

Bismuth is highly crystalline and very brittle; it has a greyish-white colour, with distinct reddish tinge, a specific gravity of 9·823 at 12°, and melts at 270°, expanding in the act of solidification. It may be obtained in a mass of very fine crystals by melting a considerable quantity, leaving it to cool till it begins to solidify, then piercing the crust, and pouring out the liquid residue. The crystals thus obtained are rhombohedrons with angles of nearly 90°, so that they present the appearance of cubes. Bismuth volatilises at a high temperature. It is remarkable as being the most diamagnetic of all known bodies. It is little oxidised by the air, but burns with a

* For further details and description of other processes, see Winckler (Bericht über die Entwickelung der chemischen Industrie, i. 953); and Roscoe and Schorlemmer's Treatise on Chemistry, vol. ii. part ii. p. 330.

bluish flame when strongly heated. Nitric acid somewhat diluted dissolves it freely.

Bismuth forms three classes of compounds, in which it is bi-, tri-, and quinqui-valent respectively. The tri-compounds are the most stable and the most numerous. The only known compounds in which bismuth is quinquivalent are indeed the pentoxide, Bi_2O_5, together with the corresponding acid and metallic salts Nevertheless, bismuth is regarded as a pentad, on account of the analogy of its compounds with those of antimony. Several bismuth compounds are known in which the metal is apparently bivalent, but really trivalent, as:

$$Bi_2Cl_4, \text{ or } \begin{matrix} BiCl_2 \\ | \\ BiCl_2 \end{matrix}; \quad Bi_2O_2, \text{ or } \begin{matrix} Bi{=}O \\ | \\ Bi{=}O \end{matrix}, \text{ \&c.}$$

Chlorides.—The *trichloride*, or *Bismuthous chloride*, is formed when bismuth is heated in a current of chlorine gas, and passes over as a white, easily fusible substance, which readily attracts moisture from the air, and is converted into a crystallised hydrate. The same substance is produced when bismuth is dissolved in nitro-muriatic acid, and the solution evaporated. Bismuthous chloride dissolves in water containing hydrochloric acid, but is decomposed by pure water, yielding a white precipitate of oxychloride:

$$BiCl_3 + H_2O = BiClO + 2HCl.$$

The *dichloride*, Bi_2Cl_4, produced by heating the trichloride with metallic bismuth, is a brown, crystalline, easily fusible mass, decomposed by water. At a high temperature it is resolved into the trichloride and metallic bismuth.

Oxides.—The *trioxide*, or *Bismuthous oxide*, is a straw-yellow powder, obtained by gently igniting the neutral or basic nitrate. It is fusible at a high temperature, and in that state acts towards siliceous matter as a powerful flux.

The *hydroxide*, $BiHO_2$ or Bi_2O_3,H_2O, is obtained as a white precipitate when a solution of the nitrate is decomposed by an alkali. Both the hydroxide and the anhydrous oxide dissolve in the stronger acids, forming the bismuthous salts, which have the composition BiR_3, where R denotes an acid radicle, *e.g.*, $BiCl_3$, $Bi(NO_3)_3$, $Bi_2(SO_4)_3$. Many of these salts crystallise well, but cannot exist in solution unless an excess of acid is present. On diluting the solutions with water, a basic salt is precipitated, and an acid salt remains in solution.

The *normal nitrate*, $Bi(NO_3)_3,5H_2O$, or $Bi_2O_3,3N_2O_5,10H_2O$, forms large transparent colourless crystals, which are decomposed by water in the manner just mentioned, yielding an acid solution containing a little bismuth, and a brilliant white crystalline powder, which varies to a certain extent in composition according to the temperature and the quantity of water employed, but frequently consists of a

Anhydrous tantalic oxide, obtained by igniting the hydroxide or sulphate, is a white powder, varying in density from 7·022 to 8·264, according to the temperature to which it has been exposed. Heated in ammonia gas it yields tantalum nitride: heated with carbon bisulphide, it is converted into tantalum bisulphide. It is insoluble in all acids, and can be rendered soluble only by fusion with potassium hydroxide or carbonate.

Tantalum Hydroxide, or *Tantalic acid*, obtained by precipitating an aqueous solution of potassium tantalate with hydrochloric acid, or by decomposing the chloride with water, is a snow-white bulky powder, which dissolves in hydrochloric and hydrofluoric acids; when strongly heated, it glows and gives off water.

Tantalic oxide unites with basic metallic oxides, forming the tantalates, which are represented by the formulæ, M_2O,Ta_2O_5 and $4M_2O,3Ta_2O_5$, the first including the native tantalates, such as ferrous tantalate, and the second certain easily crystallisable tantalates of the alkali-metals. The tantalates of the alkali-metals are soluble in water, and are formed by fusing tantalic oxide with caustic alkalis: those of the earth-metals and heavy metals are insoluble, and are formed by precipitation.

Tantalum dioxide, or *Tantalous oxide*, TaO_2, may be represented by the formula $\begin{matrix} O{=}Ta{=}O \\ | \\ O{=}Ta{=}O \end{matrix}$, in which the metal is still quinquivalent. It is produced by exposing tantalic oxide to an intense heat in a crucible lined with charcoal. It is a hard dark grey substance, which, when heated in the air, is converted into tantalic oxide.

Hydrochloric or *sulphuric acid*, added in excess to a solution of alkaline tantalate, forms a precipitate of tantalic acid, which redissolves in excess of the hydrochloric, but not of the sulphuric acid. *Potassium ferrocyanide*, added to a very slightly acidulated solution of an alkaline tantalate, forms a yellow precipitate; the *ferricyanide*, a white precipitate. *Infusion of galls* forms a light yellow precipitate, soluble in alkalis. When tantalic chloride is dissolved in strong sulphuric acid, and then water and metallic *zinc* are added, a fine blue colour is produced, which does not turn brown, but soon disappears.

Tantalic oxide fused with microcosmic salt in either blow-pipe flame forms a clear, colourless glass, which does not turn red on addition of a ferrous salt. With borax it also forms a transparent glass, which may be rendered opaque by interrupted blowing, or *flaming*.

NIOBIUM, or COLUMBIUM.

Symbol, Nb. Atomic weight, 94.

This metal, discovered in 1801 by Hatchett, in American columbite, exists likewise, associated with tantalum, in columbites from other sources, and in most tantalites; also associated with yttrium, uranium, iron, and small quantities of other metals, in Siberian samarskite, uranotantalite, or yttroilmenite; also in pyrochlore, euxenite, and a variety of pitchblende from Satersdälen in Norway.

The metal, obtained in the same manner as tantalum, is a black powder, which oxidises with incandescence when heated in the air. It dissolves in hot hydrofluoric acid, with evolution of hydrogen, and, at ordinary temperatures, in a mixture of hydrofluoric and nitric acid; slowly also when heated with strong sulphuric acid. It is oxidised by fusion with acid potassium sulphate, and gradually converted into potassium niobate by fusion with potassium hydrate or carbonate.

Niobium is quinquivalent, and forms only one class of compounds, namely, a chloride, $NbCl_5$; oxide, Nb_2O_5; oxychloride, $NbOCl_3$, &c.

Niobic Oxide, Nb_2O_5, is formed when the metal burns in the air. It is prepared from columbite, &c., by fusing the levigated mineral in a platinum crucible with 6 or 8 parts of acid potassium sulphate, removing soluble salts by boiling the fused mass with water, digesting the residue with ammonium sulphide to dissolve tin and tungsten, boiling with strong hydrochloric acid to remove iron, uranium, and other metals, and finally washing with water. As thus obtained, it is generally mixed with tantalic oxide, from which it may be separated by means of hydrogen-potassium fluoride, which converts the tantalum into sparingly soluble potassium tantalofluoride, $3KF,TaF_5$, and the niobium into easily soluble potassium nioboxyfluoride, $2KF,NbOF_3 + H_2O$.

Niobic oxide is a white amorphous infusible powder, having a density of 4·53 and becoming crystalline when strongly heated. By fusion with boric oxide or with borax, it may be obtained in prismatic crystals.

Niobium Hydroxide, or *Niobic acid*, $HNbO_3$, formed by decomposing the pentachloride or oxychloride with water, is a white powder resembling tantalic acid in its principal properties. It is slightly soluble in hot hydrochloric acid, and the solution, on addition of zinc, turns blue and yields a precipitate, probably of Nb_2O_4.

Niobates.—Some of these salts occur as natural minerals, columbite for example being a ferromanganous niobate. The *potassium niobates* crystallise readily and in well-defined forms. The *hexniobate*, $K_8Nb_6O_{19},16H_2O$ or $4K_2O,3Nb_2O_5,16H_2O$, obtained by fusing niobic oxide with twice its weight of potassium carbonate

dissolving the melt in water, and evaporating under the air-pump, forms large glistening monoclinic crystals which effloresce on exposure to the air. On adding caustic potash to the solution of this salt, and evaporating slowly, the salt $K_6Nb_4O_{13},13H_2O$, is obtained in efflorescent rhombic pyramids. By fusing niobic oxide and potassium carbonate together in molecular proportions, a crystalline mass is obtained which when treated with water yields the salt,

$$2K_2Nb_4O_{11},11H_2O \text{ or } 2(K_2O,2Nb_2O_5) + 11H_2O.$$

With a larger proportion of potassium carbonate the salt

$$K_4Nb_6O_{17},11H_2O \text{ or } 2K_2O,3Nb_2O_5 + 11H_2O,$$

is obtained.* The *sodium niobates* are crystalline powders which decompose during washing. There is also a sodium and potassium niobate, containing $Na_2O,3K_2O,3Nb_2O_5,9H_2O$.

Niobic Chloride, $NbCl_5$, is obtained, together with the oxychloride, by heating an intimate mixture of niobic oxide and charcoal in a stream of chlorine gas. It is yellow, volatile, and easily fusible. Its observed vapour-density, according to Deville and Troost, is 9·6 referred to air, or 138·6 referred to hydrogen as unity; by calculation for a two-volume condensation, it is $\frac{94+5.35{\cdot}5}{2} = 135{\cdot}75$. The *oxychloride*, $NbOCl_3$, is white, volatile, but not fusible: its density, referred to hydrogen, is by observation, 114·06; by calculation, $\frac{94+16+3.35{\cdot}5}{2} = 108{\cdot}25$. Both these compounds are converted by water into niobic oxide.

Niobic Oxyfluoride, $NbOF_3$, is formed by dissolving niobic oxide in hydrofluoric acid. It unites with the fluorides of the more basic metals, forming salts isomorphous with the titanofluorides, stannofluorides, and tungstofluorides, 1 atom of oxygen in these salts taking the place of 2 atoms of fluorine. Marignac has obtained five potassium nioboxyfluorides, all perfectly crystallised, namely:

$2KF,NbOF_3,H_2O$,	crystallising in	monoclinic plates,
$3KF,NbOF_3$	„	cuboïd forms (system undetermined),
$3KF,HF,NbOF_3$	„	monoclinic needles,
$5KF,3NbOF_3,H_2O$	„	hexagonal prisms,
$4KF,3NbOF_3,2H_2O$	„	triclinic prisms.

Potassium niobofluoride, $3KF,NbF_5$, separates in shining monoclinic needles from a solution of the first of the above-mentioned nioboxyfluorides in hydrofluoric acid. Nioboxyfluorides of ammonium, sodium, zinc, and copper have also been obtained.

* Santesson, Bull. Soc. Chim. [2], xxiv. 53.

The isomorphism of these salts with the stannofluorides, titanofluorides, and tungstofluorides, shows clearly that the existence of isomorphism between the corresponding compounds of any two elements, must not be taken as a decided proof that those elements are of equal quantivalence: for in the case now under consideration, we have isomorphous salts formed by tin and titanium which are tetrads, niobium which is a pentad, and tungsten which is a hexad.

The compounds of niobium cannot easily be mistaken for those of any other metal except tantalum. The most characteristic reactions of niobates and tantalates with liquid reagents are the following:—

	Niobates.	*Tantalates.*
Hydrochloric acid . .	White precipitate, insoluble in excess.	White precipitate, soluble in excess.
Ammonium chloride .	Precipitation slow and incomplete.	Complete precipitation as acid ammonium tantalate.
Potassium ferrocyanide	Red precipitate.	Yellow precipitate.
„ ferricyanide	Bright yellow precipitate.	White precipitate.
Infusion of galls . .	range-red precipitate.	Light yellow precipitate.

Niobic oxide, heated with borax in the outer blow-pipe flame, forms a colourless bead, which, if the oxide is in sufficient quantity, becomes opaque by interrupted blowing or flaming. In microcosmic salt it dissolves abundantly, forming a colourless bead in the outer flame, and in the inner a violet-coloured, or if the bead is saturated with the oxide, a beautiful blue bead, the colour disappearing in the outer flame.

METALS OF THE PLATINUM GROUP.

Gold.	Palladium.	Ruthenium.
Platinum.	Rhodium.	Osmium.
	Iridium.	

THESE metals may be divided into three classes, according to their behaviour with oxygen: (1.) Gold and platinum do not combine directly with oxygen under any circumstances (2.) Palladium, rhodium, and iridium, oxidise when they are heated in air or oxygen, but their oxides decompose on strong ignition into oxygen and metal. (3.) Ruthenium and osmium unite with oxygen, to form volatile oxides which do not decompose even at the highest temperatures.

GOLD.

Symbol, Au (Aurum.) Atomic weight, 196·2.

GOLD, in small quantities, is a very widely diffused metal; traces of it are constantly found in the iron pyrites of the more ancient rocks. It is always met with in the metallic state, sometimes beautifully crystallised in the cubic form, associated with quartz, iron oxide, and other substances, in regular mineral veins. The sands of various rivers have long furnished gold derived from this source, and separable by a simple process of washing; such is the *gold-dust* of commerce.* When a veinstone is wrought for gold, it is stamped to powder, and shaken in a suitable apparatus with water and mercury; an amalgam is thus formed, which is afterwards separated from the mixture and decomposed by distillation. Formerly, the chief supply of gold was obtained from the mines of Brazil, Hungary, and the Ural mountains; but California and Australia now yield by far the largest quantity. The new gold-field of British Columbia is also very productive.

Native gold is almost always alloyed with silver. The purest specimens have been obtained from Schabrowski, near Katharinenburg, in the Ural. A specimen analysed by Gustav Rose was found to contain 98·96 per cent. of gold. The Californian gold averages from 87·5 to 88·5 per cent., and the Australian from 96 to 96·6 per

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* For a description of the methods of Gold-washing and Hydraulic Gold-mining practised in California, see Roscoe and Schorlemmer's Treatise on Chemistry, vol. ii. part ii. pp. 365—369.

cent. In some specimens of native gold, as in that from Linarowski, in the Altai mountains, the percentage of gold is as low as 60 per cent., the remainder being silver.

Pure gold is obtained from its alloys by solution in nitro-muriatic acid, and precipitated with a ferrous salt, which reduces the gold and is converted into a ferric salt, thus:

$$6FeSO_4 + 2AuCl_3 = 2Fe_2(SO_4)_3 + Fe_2Cl_6 + Au_2.$$

The gold falls as a brown powder, which acquires the metallic lustre by friction.

Gold is a soft metal, having a beautiful yellow colour. It surpasses all other metals in malleability, the thinnest gold leaf not exceeding, it is said, $\frac{1}{200000}$ of an inch in thickness, while the gilding on the silver wire used in the manufacture of *gold-lace* is still thinner. It may also be drawn into very fine wire. Gold has a density of 19·5: it melts at a temperature a little above the fusing point of silver. Neither air nor water affects it in the least at any temperature; the ordinary acids fail to attack it singly. A mixture of nitric and hydrochloric acid dissolves gold, however, with ease, the active agent being the liberated chlorine.

Gold forms two series of compounds: the aurous compounds, in which it is univalent, as AuCl, Au_2O, &c., and the auric compounds, in which it is trivalent, as $AuCl_3$, Au_2O_3, &c.

Chlorides.—The *monochloride* or *Aurous chloride*, AuCl, is produced when the trichloride is evaporated to dryness, and exposed to a heat of 227° until chlorine ceases to be evolved. It forms a yellowish-white mass, insoluble in water. In contact with that liquid it is decomposed slowly in the cold, and rapidly by the aid of heat, into metallic gold and trichloride.

The *trichloride* or *Auric chloride*, $AuCl_3$, is the most important compound of gold: it is always produced when gold is dissolved in nitro-muriatic acid. The deep yellow solution thus obtained yields, by evaporation, yellow crystals of the double chloride of gold and hydrogen; when this is cautiously heated, hydrochloric acid is expelled, and the residue, on cooling, solidifies to a red crystalline mass of auric chloride, very deliquescent, and soluble in water, alcohol, and ether. Auric chloride combines with a number of metallic chlorides, forming a series of double salts, called chloroaurates, of which the general formula in the anhydrous state is $MAuCl_4$ or $MCl,AuCl_3$, M representing an atom of a monad metal. These compounds are mostly yellow when in crystals, and red when deprived of water. The *ammonium salt*, $(NH_4)AuCl_4,H_2O$, crystallises in transparent needles; the sodium salt, $NaAuCl_4,2H_2O$, in long four-sided prisms. Auric chloride also forms crystalline double salts with the hydrochlorides of many organic bases.

A mixture of auric chloride with excess of acid potassium or sodium carbonate is used for gilding small ornamental articles of copper: these are cleaned by dilute nitric acid, and then boiled in

the mixture for some time, by which means they acquire a thin but perfect coating of reduced gold.

Oxides.—The *monoxide*, or *Aurous oxide*, is produced when caustic potash in solution is poured upon the monochloride. It is a green powder, partly soluble in the alkaline liquid; the solution rapidly decomposes into metallic gold which subsides, and auric oxide which remains dissolved.

Trioxide or *Auric oxide*, Au_2O_3.—When magnesia is added to auric chloride, and the sparingly soluble aurate of magnesium is well washed and digested with nitric acid, auric oxide is left as an insoluble reddish-yellow powder, which when dry becomes chestnut-brown. It is easily reduced by heat, and by mere exposure to light; it is insoluble in oxygen-acids, with the exception of strong nitric acid, insoluble in hydrofluoric acid, easily dissolved by hydrochloric and hydrobromic acids. Alkalis dissolve it freely; indeed its acid properties are very strongly marked; it partially decomposes a solution of potassium chloride when boiled with that liquid, potassium hydroxide being produced. When digested with ammonia, it yields fulminating gold, consisting, according to Berzelius, of $Au_2O_3,4NH_3,H_2O$.

The compounds of auric oxide with alkalis are called **aurates**. The *potassium salt*, $K_2O,Au_2O_3,6H_2O$ or $KAuO_2,3H_2O$, is a crystalline salt, the solution of which is sometimes used as a bath for electro-gilding. A compound of aurate and acid sulphite of potassium, or *potassium aurosulphite*, $2(KAuO_2,4KHSO_3),H_2O$, is deposited in yellow needles when potassium sulphite is added, drop by drop, to an alkaline solution of potassium aurate.

Gold shows but little tendency to form oxygen-salts. Auric oxide dissolves in strong nitric acid, but the solution is decomposed by evaporation or dilution. A *sodio-aurous thiosulphate*, $Na_3Au(S_2O_3)_2$, $2H_2O$, is prepared by mixing the concentrated solutions of auric chloride and sodium thiosulphate, and precipitating with alcohol. It is very soluble in water, and crystallises in colourless needles. Its solution is used for fixing daguerreotype pictures. With barium chloride, it yields a gelatinous precipitate of *bario-aurous thiosulphate*, $Ba_3Au_2(S_2O_3)_4$.

Sulphides.—*Aurous sulphide*, Au_2S, is formed as a dark-brown, almost black precipitate when hydrogen sulphide is passed into a boiling solution of auric chloride. It forms sulphur-salts with the monosulphides of potassium and sodium. *Auric sulphide*, Au_2S_3, is precipitated in yellow flocks when hydrogen sulphide is passed into a cold dilute solution of auric chloride. Both these sulphides dissolve in ammonium sulphide.

The presence of gold in solution may be detected by the brown precipitate with *ferrous sulphate*, fusible before the blow-pipe to a

bead of metallic gold; also by the brownish-purple precipitate, called "Purple of Cassius," formed when *stannous chloride* is added to dilute gold solutions. The composition of this precipitate is not exactly known, but after ignition it doubtless consists of a mixture of stannic oxide and metallic gold.* It is used in enamel painting.

Oxalic acid slowly reduces gold to the metallic state: to ensure complete precipitation, the gold-solution must be digested with it for 24 hours. For the quantitative analysis of a solution containing gold and other metals, oxalic acid is in most cases a more convenient precipitant than ferrous sulphate; inasmuch as, if the quantities of the other metals are also to be determined, the presence of a large quantity of iron salt may complicate the analysis considerably.

Gold intended for coin, and most other purposes, is always alloyed with a certain proportion of silver or copper, to increase its hardness and durability: the first-named metal confers a pale greenish colour. English standard gold contains $\frac{1}{12}$ of alloy, now always copper. Gold when alloyed with copper may be estimated by fusion in a cupel with lead, in the same way as silver (p. 440). If the alloy be free from silver, the weight of the globule of gold left in the cupel will, after repeated fusions, accurately represent the quantity of gold which is present in the alloy. But if the alloy contains silver, that metal remains with the gold after cupellation. In this case the original alloy, consisting of gold, silver, and copper, is fused in the muffle, together with lead and silver; the alloy of gold and silver remaining after cupellation is then boiled with nitric acid, which dissolves the silver, the gold being left behind. By this treatment, however, an accurate separation of the two metals is obtained only when they are present in certain proportions. If the alloy contains but little silver, that metal is protected from the action of the nitric acid by the gold; and if it contains too much silver, the gold is left as a powder when the silver is dissolved out. Experience has shown that the most favourable proportions are $\frac{1}{4}$ gold to $\frac{3}{4}$ silver; the gold is then left pure, retaining the original shape of the alloy, and can be easily dried and weighed. The quantity of silver which is added to the alloy must therefore vary with the amount of gold which it contains.

Gold-leaf is made by rolling out plates of pure gold as thin as possible, and then beating them between folds of membrane with a heavy hammer, until the requisite degree of tenuity has been reached. The leaf is made to adhere to wood, &c., by size or varnish.

Gilding on copper is sometimes performed by dipping the articles into a solution of mercury nitrate, and then shaking them with a small lump of a soft amalgam of gold, which thus becomes spread over their surfaces: the articles are subsequently heated

* Graham's Elements of Chemistry, 2nd edit., vol. ii. p. 353.

to expel the mercury, and then burnished. Gilding on steel may be effected either by applying a solution of auric chloride in ether, or by roughening the surface of the metal, heating it, and applying gold-leaf with the burnisher. Gilding by electrolysis—an elegant and simple method, now rapidly superseding many of the others—has already been noticed (p. 327). The solution usually employed is obtained by dissolving oxide or cyanide of gold in a solution of potassium cyanide.

PLATINUM.

Symbol, Pt. Atomic weight, 196·7.

PLATINUM, palladium, rhodium, iridium, ruthenium, and osmium, form a group of metals, allied in some cases by properties in common, and still more closely by their natural association. *Crude platinum*, a native alloy of platinum, palladium, rhodium, iridium, and a little iron, occurs in grains and rolled masses, sometimes of tolerably large dimensions, mixed with gravel and transported materials, on the slope of the Ural Mountains in Russia, also in Brazil, Ceylon, and a few other places. It has never been seen in the rock, which, however, is judged from the accompanying materials to have been serpentine. It is stated to be always present in small quantities with native silver.

From this substance platinum is prepared by the following process:—The crude metal is acted upon as far as possible by *aqua regia* containing an excess of hydrochloric acid and slightly diluted with water, in order to dissolve as small a quantity of iridium as possible: to the deep yellowish-red and highly acid solution thus produced, sal-ammoniac is added, by which nearly the whole of the platinum is thrown down in the state of ammonium platinochloride. This substance, washed with a little cold water, dried, and heated to redness, leaves metallic platinum in the spongy state. This metal cannot be fused into a compact mass by ordinary furnace-heat, but the same object may be accomplished by taking advantage of its property of welding, like iron, at a high temperature. The spongy platinum is made into a thin uniform paste with water, introduced into a slightly conical mould of brass, and subjected to a graduated pressure, by which the water is squeezed out, and the mass at length rendered sufficiently solid to bear handling. It is then dried, very carefully heated to whiteness, and hammered, or subjected to powerful pressure. If this operation is properly conducted, the platinum will then be in a state to bear forging into a bar, which can afterwards be rolled into plates, or drawn into wire, at pleasure.

A method of refining platinum has been devised by Deville and Debray, consisting in submitting the crude metal to the action of an intensely high temperature in a crucible of lime. The apparatus they employ is as follows:—The lower part of the furnace consists

of a piece of lime, hollowed out in the centre to the depth of about a quarter of an inch ; a small notch is filed at one side of this basin, through which the metal is introduced and poured out. A cover made of another piece of lime fits on the top of this basin ; it is also hollowed to a small extent, and has a conical perforation at the top, into which is inserted the nozzle of an oxy-hydrogen blow-pipe. The whole arrangement is firmly bound with iron wire. To use the apparatus, the stop-cock supplying the hydrogen (or coal gas) is opened, and the gas lighted at the notch in the crucible ; the oxygen is then gradually supplied ; and when the furnace is sufficiently hot, the metal is introduced in small pieces through the orifice. By this arrangement as much as 50 pounds of platinum and more may be fused at once. All the impurities in the platinum, except the iridium and rhodium, are separated in this manner : the gold and palladium are volatilised ; the sulphur, phosphorus, arsenic, and osmium oxidised and volatilised ; and the iron and copper are oxidised and absorbed by the lime of the crucible.

Platinum is a little whiter than iron : it is exceedingly malleable and ductile, both hot and cold, and is very difficult to fuse, melting only before the oxy-hydrogen blow-pipe, or in the powerful blast furnace just described. It is the heaviest substance known, except osmium, its specific gravity being 21·5. Neither air, moisture, nor the ordinary acids attack platinum in the slightest degree at any temperature : hence its great value in the construction of chemical vessels. It is dissolved by *aqua regia*, and superficially oxidised by fused potassium hydroxide, which enters into combination with the oxide.

The remarkable property of the spongy metal to determine the union of oxygen and hydrogen has been already noticed (p. 162). There is a still more curious state in which platinum can be obtained —that of *platinum-black*, in which the division is carried much further. It is easily prepared by boiling a solution of platinic chloride to which an excess of sodium carbonate and a quantity of sugar have been added, until the precipitate formed after a little time becomes perfectly black, and the supernatant liquid colourless. The black powder is collected on a filter, washed, and dried by gentle heat. This substance appears to possess the property of condensing gases, more especially oxygen, into its pores to a very great extent : when placed in contact with a solution of formic acid, it converts the latter, with copious effervescence, into carbonic acid ; alcohol, dropped upon the platinum-black, becomes changed by oxidation to acetic acid, the rise of temperature being often sufficiently great to cause inflammation. When exposed to a red heat, the black substance shrinks in volume, assumes the appearance of common spongy platinum, and loses these peculiarities, which are no doubt the result of its excessively comminuted state.

Platinum forms two series of compounds : the platinous compounds, in which it is bivalent, *e.g.*, $PtCl_2$, PtO, and the platinic compounds, in which it is quadrivalent, *e.g.*, $PtCl_4$, PtO_2, &c.

Chlorides.—The *dichloride*, or *Platinous chloride*, $PtCl_2$, is produced when platinic chloride, dried and powdered, is exposed for some time to a heat of about 200°, whereby half the chlorine is expelled; also, when sulphurous acid gas is passed into a solution of the tetrachloride until the latter ceases to give a precipitate with sal-ammoniac. It is a greenish-grey powder, insoluble in water, but dissolved by hydrochloric acid. The latter solution, mixed with sal-ammoniac or potassium chloride, deposits a double salt in fine red prismatic crystals, containing, in the last case, K_2PtCl_4 or $2KCl,PtCl_2$. The corresponding sodium compound is very soluble, and difficult to crystallise. These double salts are called *platinoso-chlorides* or *chloroplatinites*. Platinous chloride is decomposed by heat into chlorine and metallic platinum.

Platinous chloride unites with carbon monoxide, forming the three compounds

$$Cl_2Pt{=}CO, \qquad Cl_2Pt\begin{matrix}CO\\|\\CO\end{matrix}, \qquad Cl_2Pt\begin{matrix}CO{-}PtCl_2\\|\\CO{-}CO\end{matrix},$$

all of which are produced by heating platinous chloride in a stream of carbon monoxide. The first and third crystallise in yellow needles, the second in white needles.

Platinous chloride also unites with phosphorus trichloride, forming phospho-platinic chloride, $Cl_2Pt{=}PCl_3$, which is obtained by heating spongy platinum with phosphorus pentachloride to 250°. It crystallises in maroon-coloured needles, melting at 170°. When heated with excess of phosphorus trichloride, it is converted into diphosphoplatinic chloride, $Cl_2Pt\begin{matrix}PCl_3\\|\\PCl_3\end{matrix}$, which forms canary-yellow crystals melting at 160°. These two chlorides are converted by water—the latter on exposure to moist air at a low winter temperature—into phosphoplatinic and diphosphoplatinic acids, $Cl_2Pt{=}P(OH)_3$ and $Cl_2Pt\begin{matrix}P(OH)_3\\|\\P(OH)_3\end{matrix}$, the former of which is tribasic, the latter sexbasic.

Platinum tetrachloride, or *Platinic chloride*, $PtCl_4$, is always formed when platinum is dissolved in *aqua regia*. The acid solution yields, on evaporation to dryness, a red or brown residue, deliquescent, and very soluble both in water and in alcohol; the aqueous solution has a pure orange-yellow tint. Platinic chloride unites with a great variety of metallic chlorides, forming double salts called *platino-chlorides* or *chloro-platinates*; the most important of these compounds are those containing the metals of the alkalis, and ammonium. *Potassium platinochloride*, $2KCl,PtCl_4$, or K_2PtCl_6, the platinum being octovalent, forms a bright yellow crystalline precipitate, being produced whenever solutions of the chlorides of platinum and of potassium are mixed, or a potassium salt

mixed with a little hydrochloric acid is added to platinum tetrachloride. It is feebly soluble in water, still less soluble in dilute alcohol, and is decomposed with some difficulty by heat. It is easily reduced by hydrogen at a high temperature, yielding a mixture of potassium chloride and platinum-black: the latter substance may thus, indeed, be very easily prepared. The *sodium salt*, $2NaCl,PtCl_4,6H_2O$, or $Na_2PtCl_6,6H_2O$, is very soluble, crystallising in large, transparent, yellow-red prisms. The *ammonium salt*, $2NH_4Cl,PtCl_4$, is undistinguishable, in physical characters, from the potassium-salt; it is thrown down as a precipitate of small, transparent, yellow, octohedral crystals when sal-ammoniac is mixed with platinic chloride; it is but feebly soluble in water, still less so in dilute alcohol, and is decomposed by heat, yielding spongy platinum, while sal-ammoniac, hydrochloric acid, and nitrogen are driven off. Platinic chloride also forms crystallisable double salts with the hydrochlorides of many organic bases; with ethylamine, for example, the compound,

$$2[NH_2(C_2H_5),HCl]_2PtCl_4 \text{ or } [NH_3(C_2H_5)_2]_2PtCl_6.$$

The *bromides* and *iodides of platinum* are analogous in composition to the *chlorides*, and likewise form double salts with alkaline bromides and iodides.

Oxides.—The *monoxide*, or *Platinous oxide*, PtO, is obtained by digesting the dichloride with caustic potash, as a black powder, soluble in excess of alkali. It dissolves also in acids with brown colour, and the solutions are not precipitated by sal-ammoniac. When platinum dioxide is heated with solution of oxalic acid, it is reduced to monoxide, which remains dissolved. The liquid has a dark blue colour, and deposits fine copper-red needles of platinous oxalate.

The *dioxide*, or *Platinic oxide*, PtO_2, is best prepared by adding barium nitrate to a solution of platinic sulphate; barium sulphate and platinic nitrate are then produced, and from the latter caustic soda precipitates one-half of the platinum as *platinic hydroxide*. The sulphate is itself obtained by acting with strong nitric acid upon platinum bisulphide, which falls as a black powder when a solution of the tetrachloride is dropped into potassium sulphide. Platinic hydroxide is a bulky brown powder, which, when gently heated, becomes black and anhydrous. It may also be formed by boiling platinic chloride with a great excess of caustic soda, and then adding acetic acid. It dissolves in acids, and combines with bases: the salts have a yellow or red tint, and a great disposition to unite with salts of the alkalis and alkaline earths, giving rise to a series of double compounds, which are not precipitated by excess of alkali. A combination of platinic oxide with ammonia exists, which is explosive. Both oxides of platinum are reduced to the metallic state by ignition.

Sulphides.—The compounds PtS and PtS_2, are produced by the action of hydrogen sulphide, or the hydrosulphide of an alkali-metal, on the dichloride and tetrachloride of platinum respectively; they are both black substances, insoluble in water. Platinic sulphide heated in a close vessel gives off half its sulphur, and is reduced to platinous sulphide. It dissolves in alkaline hydroxides, carbonates, and sulphides, forming salts called *thioplatinates*, which are decomposed by acids.

Ammoniacal Platinum Compounds.—The chlorides, oxides, sulphates, &c., of platinum are capable of taking up two or more molecules of ammonia, and forming compounds analogous in many respects to the ammoniacal mercury compounds already described.

The nitrogen in all these compounds is quinquivalent, and consequently the groups *ammonia*, NH_3, and *diammonia*, N_2H_6 or $NH_3—NH_3$ or $NH_2(NH_4)$, are bivalent, having two free combining units.

The platinum in some of these compounds is bivalent (*plato* or *platoso*), and unites by two of its combining units with the bivalent groups, NH_3 or N_2H_6, each of which retains one combining unit free. In others the platinum is quadrivalent (*platino*), and unites by some of its combining units with ammonia or diammonia, the remaining units being satisfied by combination with electro-negative radicles. In others, again, the platinum accumulates in such a manner as to form compounds containing $(Pt_2)''$, $(Pt^{iv}—Pt^{iv})^{vi}$, $(Pt^{iv}—Pt^{iv}—Pt^{iv}—Pt^{iv})^{x}$, &c. The bivalent groups, NH_3, N_2H_6, always go by pairs, excepting in the semi-diammoniums, in which half or a quarter of the combining units of the platinum is satisfied by once N_2H_6.

The names and constitution of the several groups are given in the following table, the symbol R denoting a univalent chlorous radicle, such as Cl, NO_2, &c.

1. Platosammonium compounds, $Pt<^{NH_3R}_{NH_3R}$
2. Platosemidiammonium compounds, $Pt<^{NH_2(NH_4)R}_{R}$
3. Platomonodiammonium compounds, $Pt<^{NH_2(NH_4)R}_{NH_3R}$
4. Platosodiammonium compounds, $Pt<^{NH_2(NH_4)R}_{NH_2(NH_4)R}$
5. Platinammonium compounds, $R_2Pt<^{NH_3R}_{NH_3R}$
6. Platinosemidiammonium compounds, $R_2Pt<^{NH_2(NH_4)R}_{R}$

7. Platinomonodiammonium compounds, $R_2Pt<^{NH_3R}_{NH_2(NH_4)R}$

8. Platinodiammonium compounds, $R_2Pt<^{NH_2(NH_4)R}_{NH_2(NH_4)R}$

9. Diplatinammonium compounds, $\begin{matrix} RPt<^{NH_3R}_{NH_3R} \\ | \\ RPt<^{NH_3R}_{NH_3R} \end{matrix}$

10. Diplatosodiammonium compounds, $\begin{matrix} Pt—NH_2(NH_4)R \\ | \\ Pt—NH_2(NH_4)R \end{matrix}$

11. Diplatinodiammonium compounds, $\begin{matrix} R_2Pt—NH_2(NH_4)R \\ | \\ R_2Pt—NH_2(NH_4)R \end{matrix}$

12. Diplatinotetradiammonium compounds, $\begin{matrix} RPt<^{NH_2(NH_4)R}_{NH_2(NH_4)R} \\ | \\ RPt<^{NH_2(NH_4)R}_{NH_2(NH_4)R} \end{matrix}$

We shall here describe the most characteristic compounds of each group, referring for more complete description to larger works.*

1. *Platosammonium Compounds.*—These compounds are formed by abstraction of the elements of ammonia, NH_3, from the corresponding platosodiammonium-compounds. They are for the most part insoluble in water, but dissolve in ammonia, reproducing the platosodiammonium-compounds. They detonate when heated.

The *chloride*, $Pt<^{NH_3Cl}_{NH_3Cl}$ or $N_2H_6PtCl_2$, is formed by heating platosodiammonium chloride to 220—270°, or by heating the same salt with hydrochloric acid, or by boiling the green salt of Magnus (p. 555) with nitrate or sulphate of ammonium, and is deposited as a yellow crystalline powder, or in rhombohedral scales. It dissolves in 4472 parts of water at 0° and in 130 parts of boiling water. At 270° it decomposes in the manner represented by the equation,

$$3N_2H_6PtCl_2 = 3Pt + 4NH_4Cl + 2HCl + N_2.$$

Silver nitrate added to its solution throws down all the chlorine. This salt is isomeric with the green salt of Magnus, with the yellow chloride of platosemidiammonium, and with the chloroplatinite of platosomonodiammonium.

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* See Watts's Dictionary of Chemistry, iv. 673, and 2nd Suppl. 992.

The corresponding *iodide*, $N_2H_6PtI_2$, is a yellow powder, obtained by heating the aqueous solution of the compound $N_4H_{12}PtI_2$. It dissolves in ammonia, reproducing the latter compound. The *oxide*, N_2H_6PtO, obtained by heating platosodiammonium oxide (p. 555) to 110°, is a greyish mass, which, when heated to 100° in a close vessel, gives off water, ammonia, and nitrogen, and leaves metallic platinum. The *hydroxide*, $N_2H_6Pt(HO)_2$, obtained by decomposing the sulphate with baryta-water, is a strong base, soluble in water, having an alkaline reaction, absorbing carbonic acid from the air, and liberating ammonia from its salts (Odling). The *sulphate*, $N_2H_6PtSO_4,H_2O$, and the *nitrate*, $N_2H_6Pt(NO_3)_2$, are obtained by boiling the iodide with sulphate and nitrate of silver: they are crystalline, and have a strong acid reaction. The sulphate retains a molecule of crystallisation-water, which cannot be removed without decomposing the salt.

2. *Platososemidiammonium Compounds.* — These compounds, isomeric with the preceding, are formed by direct addition of ammonia to platinous salts. The *chloride*, $Pt<^{N_2H_6Cl}_{Cl}$, is obtained by adding ammonia to a cold solution of platinous chloride in hydrochloric acid, filtering after 24 hours, and treating the yellowish-green residue with boiling water, which dissolves the platosemidiammonium salt, and leaves the green salt of Magnus formed at the same time. The solution on cooling deposits the platososemidiammonium chloride in small prisms, differing in form from the chloride above described, and much more soluble in water, requiring for solution 387 parts of cold and 26 parts of boiling water. The other salts of this base are obtained by decomposing the chloride with the corresponding silver salts. The *bromide* and *iodide* crystallise in yellow needles; the *nitrite* in silky needles, which detonate when heated; the *nitrate* and *sulphate* form yellowish crystalline crusts.

3. *Platosomonodiammonium Compounds*, $Pt<^{N_2H_6R}_{NH_3R}$. — The *chloroplatinite* of this series, $2N_3H_9PtCl_2,PtCl_2$, formed in small quantity on adding ammonia to a solution of platinous chloride, crystallises in brown square laminæ, slightly soluble in cold, more soluble in boiling water. Treated with silver nitrate it is converted into platosomonodiammonium *nitrate*, and this, when heated with hydrochloric acid, yields the corresponding *chloride*, $N_3H_9PtCl_2$, which is very soluble, and crystallises in colourless needles or nacreous scales.

4. *Platosodiammonium Compounds*, $Pt<^{N_2H_6R}_{N_2H_6R}$. — The *chloride*, $N_4H_{12}PtCl_2$, one of the earliest discovered of the ammoniacal platinum compounds, is obtained by the action of ammonia on the green salt of Magnus, or on the chloride of platosammonium. When platinous chloride is boiled with excess of ammonia till the

green precipitate formed in the first instance is redissolved, a solution is obtained, which, when filtered and evaporated, yields the chloride of platosodiammonium in splendid yellow crystals containing one molecule of water, which they give off at 110°. It is soluble in water, and its solution mixed with platinous chloride yields *platosodiammonium chloroplatinite*, $N_4H_{12}PtCl_2,PtCl_2$, isomeric with platosammonium chloride, and constituting the *green salt of Magnus*, the first discovered of the ammonia-platinum compounds. This last salt may also be prepared by passing sulphurous acid gas into a boiling solution of platinic chloride till it is completely converted into platinous chloride (and is therefore no longer precipitated by sal-ammoniac), and neutralising the solution with ammonia. It forms dark green needles, insoluble in water, alcohol, and hydrochloric acid.

The *bromide* and *iodide* of this series are obtained by treating the solution of the sulphate with bromide or iodide of barium: they crystallise in cubes. The *oxide*, $N_4H_{12}PtO$, is obtained as a crystalline mass by decomposing the solution of the sulphate with an equivalent quantity of baryta-water, and evaporating the filtrate in a vacuum. It is strongly alkaline and caustic, like potash, absorbs carbonic acid rapidly from the air, and precipitates silver oxide from the solution of the nitrate. It is a strong base, neutralising acids completely, and expelling ammonia from its salts. It melts at 110°, giving off water and ammonia, and leaving platosammonium oxide. Its aqueous solution does not give off ammonia, even when boiled. The oxide absorbs carbon dioxide rapidly from the air, forming first a normal carbonate, $N_4H_{12}PtCO_3,H_2O$, and afterwards an acid salt, $N_4H_{12}PtCO_3,H_2CO_3$. The *sulphate*, $N_4H_{12}PtSO_4$, and the *nitrate*, $N_4H_{12}Pt(NO_3)_2$, are obtained by decomposing the chloride with silver sulphate or nitrate; they are neutral, and crystallise easily.

5. *Platinammonium Compounds.*—The chloride, $Cl_2Pt<\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}$, is obtained by the action of chlorine on platosammonium chloride suspended in boiling water. It is a lemon-yellow crystalline powder, made up of quadratic octohedrons with truncated summits. It is insoluble in cold water, very slightly soluble in boiling water, or in water containing hydrochloric acid. It dissolves in ammonia at a boiling heat, and the solution, on cooling, deposits a yellow precipitate, consisting of platinodiammonium chloride. It dissolves in boiling potash without evolving ammonia.

Nitrates.—An *oxynitrate*, $N_2H_6Pt(NO_3)_2O$, is obtained by boiling the chloride, $N_2H_6PtCl_4$, for several hours with dilute silver nitrate. It is a yellow crystalline powder, sparingly soluble in cold, more soluble in boiling water. The *normal nitrate*, $N_2H_6Pt(NO_3)_4$, is obtained by dissolving the oxynitrate in nitric acid: it is yellowish, insoluble in cold water, soluble in hot nitric acid.

The *oxide*, $N_2H_6PtO_2$, is obtained by adding ammonia to a boiling solution of platinammonium nitrate; it is then precipitated in the form of a heavy, yellowish, crystalline powder, composed of small shining rhomboidal prisms; it is nearly insoluble in boiling water, and resists the action of boiling potash. Heated in a close vessel, it gives off water and ammonia, and leaves metallic platinum. It dissolves readily in dilute acids, even in acetic acid, and forms a large number of crystallisable salts, both neutral and acid, having a yellow colour, and sparingly soluble in water. Another compound of platinic oxide with ammonia, called *fulminating platinum*, whose composition has not been exactly ascertained, is produced by decomposing ammonium platino-chloride with aqueous potash. It is a straw-coloured powder, which detonates slightly when suddenly heated, but strongly when exposed to a gradually increasing heat.

6. *Platinosemidiammonium Compounds.*—Isomeric with the preceding. The *chloride*, $Cl_2Pt<^{N_2H_6Cl}_{Cl}$, formed by the action of chlorine on platososemidiammonium chloride, crystallises in yellow six-sided plates belonging to the rhombic system, turning green at 100°, and dissolving in potash without evolution of ammonia. A *basic nitrate*, $(OH)_2Pt<^{N_2H_6—NO_3}_{OH}$, is obtained as an amorphous yellow precipitate by treating the chloride with silver nitrate. A *chloronitrate*, $Cl_2Pt<^{N_2H_6.NO_2}_{NO_2}$, obtained by the action of chlorine on platososemidiammonium nitrate, crystallises in small yellow needles.

7. *Platinomonodiammonium Compounds.*—The *chloride*, $Cl_2Pt<^{N_2H_6Cl}_{NH_3Cl}$, formed by the action of nitro-muriatic acid on platosomonodiammonium chloride, crystallises in rhombic or hexagonal plates. A *bromonitrate*, $Br_2Pt<^{N_2H_6(NO_3)}_{NH_3(NO_3)} + H_2O$, obtained by adding bromine to the nitrate of platosomonodiammonium, forms yellow soluble crusts.

8. *Platinodiammonium Compounds.* — The chloride, $PtCl_2<^{N_2H_6Cl}_{N_2H_6Cl}$, is obtained by passing chlorine gas into a solution of platosodiammonium chloride; by dissolving platinammonium chloride in ammonia, and expelling the excess of ammonia by evaporation; or by precipitating a solution of platinodiammonium oxynitrate, or nitratochloride, with hydrochloric acid. It is white, and dissolves in small quantity in boiling water, from which solution it is deposited in the form of transparent regular octohedrons, having a faint yellow tint. When a solution of this salt is treated with silver nitrate, one-half of the chlorine is very easily precipitated,

but to remove even a small portion of the remainder requires a long-continued action of the silver-salt. The *chlorobromide*, $\begin{matrix}Br\\Cl\end{matrix}>Pt<\begin{matrix}N_2H_6Br\\N_2H_6Cl\end{matrix}$, is obtained as a yellow precipitate by treating platinodiammonium chloride with bromine. A *basic nitrate*, $\begin{matrix}HO\\NO_3\end{matrix}>Pt<\begin{matrix}N_2H_6.NO_3\\N_2H_6.NO_3\end{matrix}$, is obtained by the action of nitric acid on platosodiammonium nitrate, as a white crystalline powder, converted by ammonia into the salt $(HO)_2Pt(N_2H_6.NO_3)_2$. The *sulphatochloride*, $Cl_2Pt<\begin{matrix}N_2H_6\\N_2H_6\end{matrix}>SO_4$, formed by the action of sulphuric acid on the chloride, crystallises in slender transparent needles. An *oxalochloride*, $Cl_2Pt(N_2H_6)_2C_2O_4$, obtained by treating the chloride with ammonium oxalate, is a very soluble crystalline powder.

9. *Diplatinammonium Iodide*, $\begin{matrix}IPt(NH_3I)_2\\|\\IPt(NH_3I)_2\end{matrix}$, or $I_2(Pt_2)^{vi}(NH_3I)_4$, the only term of this series at present known, is obtained by treating platosammonium iodide with boiling potash, and the resulting yellow powder with hydriodic acid. It is a black amorphous substance, which when again treated with potash and hydriodic acid, yields the compound $I_2(Pt_4)^x(NH_3I)_8$, and this by similar treatment may be converted into the still more condensed compound $I_2(Pt_8)^{xviii}(NH_3I)_{16}$.

10. *Diplatosodiammonium Compounds.*—The *hydroxide*, $\begin{matrix}Pt—N_2H_6—OH\\|\\Pt—N_2H_6—OH\end{matrix}$, formed by the action of caustic soda on the chloride of platososemidiammonium, is a greyish crystalline insoluble powder, which detonates violently when heated. Treated with hydrochloric acid, it yields a yellow powder, which is converted by boiling water into the *chloride*, $Pt_2(N_2H_6Cl)_2$.

11. *Diplatinodiammonium Chloride*, $\begin{matrix}Cl_2Pt—NH_3—NH_2\\|\\Cl_2Pt—NH_3—NH_2\end{matrix}$, is a yellow amorphous powder formed by the action of nitro-muriatic acid on the hydroxide of the preceding series.

12. *Diplatino-tetradiammonium Compounds*, $\begin{matrix}RPt(N_2H_6R)_2\\|\\RPt(N_2H_6R)_2\end{matrix}$ or $N_8H_{24}Pt_2R_6$. An *oxynitrate*, $O\begin{matrix}Pt(N_2H_6.NO_3)_2\\|\\Pt(N_2H_6.NO_3)_2\end{matrix}$ or $N_8H_{24}Pt_2(NO_3)_4O$, is produced by boiling platosodiammonium nitrate with nitric acid. It is a colourless, crystalline, detonating salt, slightly soluble in cold water, more soluble in boiling water, insoluble in nitric acid (Gerhardt). A *nitratoxychloride*,

$N_8H_{24}Pt_2(NO_3)_4OCl_2$, discovered by Raewsky, is formed when Magnus's green salt is boiled with a large excess of nitric acid. Red fumes are then evolved, and the resulting solution deposits the nitrat-oxychloride in small brilliant needles, which deflagrate when heated, giving off water and sal-ammoniac, and leaving metallic platinum. The nitric acid in this salt may be replaced by an equivalent quantity of carbonic or oxalic acid, yielding the compounds, $N_8H_{24}Pt_2(CO_3)_2OCl_2$, and $N_8H_{24}Pt_2(C_2O_4)_2OCl_2$, both of which are crystallisable, and sparingly soluble. A *basic oxalo-nitrate*, $N_8H_{24}Pt_2(C_2O_4)_2(NO_3)_2O$, insoluble in water, is obtained by adding ammonium oxalate to the oxynitrate.

Reactions of Platinum Salts.—Platinic chloride, or a platinic oxygen-salt, may be recognised in solution by the yellow precipitate which it forms with *sal-ammoniac*, decomposible by heat, with production of spongy metal.

Hydrogen sulphide and *ammonium sulphide* gradually form a brown precipitate of platinic sulphide, soluble in excess of ammonium sulphide. *Zinc* precipitates metallic platinum.

Platinic chloride and sodium platinochloride are employed in analytical investigations to detect the presence of potassium and separate it from sodium. For the latter purpose, the alkaline salts are converted into chlorides, and in this state mixed with four times their weight of sodium platinochloride in crystals, the whole being dissolved in a little water. When the formation of the yellow salt appears complete, alcohol is added, and the precipitate collected on a weighed filter, washed with weak spirit, carefully dried, and weighed. The potassium chloride is then easily reckoned from the weight of the double salt ; and this, subtracted from the weight of the mixed chlorides employed, gives that of the sodium chloride by difference ; 100 parts of potassium platinochloride correspond with 30·55 parts of potassium chloride.

Capsules and crucibles of platinum are of great value to the chemist ; the latter are constantly used in mineral analysis for fusing siliceous matter with alkaline carbonates. They suffer no injury in this operation, although caustic alkali roughens and corrodes the metal. The experimenter must be particularly careful to avoid introducing any oxide of an easily fusible metal, as that of lead or tin, into a platinum crucible. If reduction should by any means occur, these metals will at once alloy themselves with the platinum, and the vessel will be destroyed. A platinum crucible must never be put naked into a coke or charcoal fire, but always placed within a covered earthen crucible.

PALLADIUM.

Symbol, Pd. Atomic weight, 106·2.

When the solution of crude platinum, from which the greater part of that metal has been precipitated by sal-ammoniac, is neutralised by sodium carbonate, and mixed with a solution of mercuric cyanide, palladium cyanide separates as a whitish insoluble substance, which, on being washed, dried, and heated to redness, yields metallic palladium in a spongy state. The palladium may then be welded into a mass, in the same manner as platinum.

Palladium closely resembles platinum in colour and appearance; it is also very malleable and ductile. Its density differs very much from that of platinum, being only 11·4. Palladium is more oxidable than platinum. When heated to redness in the air, especially in the state of sponge, it acquires a blue or purple superficial film of oxide, which is reduced at a white heat. Palladium is slowly attacked by nitric acid; its best solvent is nitro-muriatic acid.

Palladium is remarkable for its power of occluding hydrogen. When heated to redness in a stream of that gas, or brought in contact with nascent hydrogen, as when made to form the negative electrode in an electrolytic cell containing acidulated water, it can absorb as much as 643 times its volume of the gas, whereby its specific gravity is reduced to 11·06.

The absorption of the gas is attended with evolution of heat, and from this fact, together with the supposed constancy of composition of the hydrogenised palladium, it has been inferred that this product is a definite chemical compound; but this view can scarcely be regarded as satisfactorily demonstrated; at all events Graham assigned to the supposed compound the formula PdH_2, whereas according to Troost and Hautefeuille, it is Pd_2H.*

Palladium, like platinum, forms two classes of compounds; namely, the palladious compounds, in which it is bivalent, and the palladic compounds, in which it is quadrivalent.

Chlorides.—The *dichloride*, or *Palladious chloride*, $PdCl_2$, is obtained by dissolving the metal in nitro-muriatic acid, and evaporating the solution to dryness. It is a dark-brown mass, which dissolves in water if the heat has not been too great, and forms double salts with many metallic chlorides. The palladio-chlorides of ammonium and potassium are much more soluble than the corresponding platinochlorides: they have a brownish-yellow tint.

The *tetrachloride*, or *Palladic chloride*, $PdCl_4$, exists only in solution and in combination with the alkaline chlorides. It is formed when the dichloride is digested in nitro-muriatic acid. The

* Watts's Dictionary of Chemistry, vi. 634; vii. 658.

solution has a deep brown colour, and is decomposed by evaporation. Mixed with potassium chloride, or with sal-ammoniac, it gives rise to a red crystalline precipitate, which is but slightly soluble in water.

Palladious Iodide, PdI_2, is precipitated from the chloride or nitrate by soluble iodides, as a black mass, which gives off its iodine between 300° and 360°. Palladium-salts are employed for the quantitative estimation of iodine, and its separation from chlorine and bromine, which are not precipitated by them.

Oxides.—The *monoxide*, or *Palladious oxide*, PdO, is obtained by evaporating to dryness, and cautiously heating the solution of palladium in nitric acid. It is black, and but little soluble in acids. The hydroxide falls as a dark-brown precipitate when sodium carbonate is added to the above solution. It is decomposed by a strong heat.

The *dioxide*, or *Palladic oxide*, PdO_2, is not known in the separate state. From a solution of palladic chloride, alkalis and alkaline carbonates throw down a brown precipitate, consisting of hydrated palladic oxide combined with the alkali. This compound gives off half its oxygen at a moderate heat, and the whole at a higher temperature. From hot solutions a black precipitate is obtained, containing the anhydrous dioxide. The hydroxide dissolves slowly in acids, forming yellow solutions. In strong hydrochloric acid it dissolves without decomposition, forming *potassio-palladic chloride*, arising from admixed potash; with dilute hydrochloric acid, on the contrary, it gives off chlorine.

Palladious Sulphide, PdS, is formed by fusing the metal with sulphur, or by precipitating a solution of a palladious salt with hydrogen sulphide. It is insoluble in ammonium sulphide.

Ammoniacal Palladium Compounds.—A moderately concentrated solution of palladium dichloride, treated with a slight excess of ammonia, yields a beautiful flesh-coloured or rose-coloured precipitate, consisting of $N_2H_6PdCl_2$. This precipitate dissolves in a large excess of ammonia; and the ammoniacal solution, when treated with acids, yields a yellow precipitate having the same composition. This yellow modification is likewise obtained by heating the red compound in the moist state to 100°, or in the dry state to 200°. The yellow compound dissolves abundantly in aqueous potash, forming a yellow solution, but without giving off ammonia, even when the liquid is heated to the boiling-point; the red compound behaves in a similar manner, but, before dissolving, is converted into the yellow modification. These compounds, discovered by Hugo Müller,* are analogous in their modes of formation, and pro-

* Ann. Ch. Pharm., lxxxvi. 341.

bably therefore in constitution, to the two modifications of the platinum compound, $N_2H_6PtCl_2$ (pp. 553, 554); the red compound being *palladiosemidiammonium chloride*, $Cl.Pd.NH_2(NH_4)Cl$, and the yellow compound, *palladammonium chloride*, $Pd(NH_3Cl)_2$. The yellow compound, digested with water and silver oxide, yields *palladammonium oxide*, N_2H_6PdO, which is a strong base, soluble in water, having an alkaline taste and reaction, and absorbing carbonic acid from the air. *Palladammonium sulphite*, $N_2H_6PdSO_3$, is formed by the action of sulphurous acid on the oxide or chloride; it crystallises in orange-yellow octohedrons. The *sulphate*, *chloride*, *iodide*, and *bromide* have likewise been formed.

The compound $(NH_3)_4PdCl_2$, or *Palladiodiammonium chloride*, $Pd[NH_2(NH_4)Cl]_2$, separates from an ammoniacal solution of palladammonium chloride in oblique rhombic prisms.

The *oxide*, $N_4H_{12}PdO$, obtained by decomposing the solution of this chloride with silver oxide, is also a strong base yielding crystallisable salts.

Palladious salts are well marked by the pale yellowish-white precipitate which they form with solution of mercuric cyanide. It consists of palladious cyanide, $PdCy_2$, and is converted by heat into the spongy metal.

Hydriodic acid and *potassium iodide* throw down a black precipitate of palladium iodide, visible even to the 500,000th degree of dilution.

Palladium, on account of its unalterability in the air, and its bright silver-white colour, which is not affected by exposure to sulphuretted hydrogen, is used for preparing the graduated surfaces of astronomical instruments, and for coating silver goods.

An amalgam of palladium is used by dentists for stopping teeth.

A native alloy of gold with palladium is found in Brazil.

RHODIUM.

Symbol, Rh. Atomic weight, 104·1.

THE solution from which platinum and palladium have been separated, in the manner already described, is mixed with hydrochloric acid, and evaporated to dryness. The residue is treated with alcohol, of specific gravity 0·837, which dissolves everything except the double chloride of rhodium and sodium. This is well washed with spirit, dried, heated to whiteness, and then boiled with water, whereby sodium chloride is dissolved out, and metallic rhodium remains. Thus obtained, rhodium is a white, coherent,

spongy mass, still less fusible and less capable of being welded than platinum. Its specific gravity is 12·1.

Rhodium is very brittle: reduced to powder and heated in the air, it becomes oxidised, and the same alteration happens to a greater extent when it is fused with nitrate or bisulphate of potassium. None of the acids, singly or conjoined, dissolve this metal, unless it be in the state of alloy, as with platinum, in which state it is attacked by nitro-muriatic acid.

Rhodium forms but one chloride, containing $RhCl_3$, in which, like iron in ferric chloride, it may be regarded as either tri- or quadrivalent. This chloride is prepared by adding silicofluoric acid to the double chloride of rhodium and potassium, evaporating the filtered solution to dryness, and dissolving the residue in water. It forms a brownish-red deliquescent mass, soluble in water, with a fine red colour. It is decomposed by heat into chlorine and metallic rhodium.

Rhodium and Potassium Chlorides.—The salt, $K_6Rh_2Cl_{12},6H_2O$, formed by mixing a solution of rhodic oxide in hydrochloric acid with a strong solution of potassium chloride, crystallises in sparingly soluble efflorescent prisms. Another double salt, containing $K_3Rh_2Cl_{10},2H_2O$, is prepared by heating in a stream of chlorine a mixture of equal parts of finely powdered metallic rhodium and potassium chloride. The salt has a fine red colour, is soluble in water, and crystallises in four-sided prisms. *Rhodium and sodium chloride*, $Na_6Rh_2Cl_{12},24H_2O$, is also a very beautiful red salt, prepared like the last. The *ammonium salt*, $(NH_4)_6Rh_2Cl_{12},3H_2O$, obtained by decomposing the sodium salt with sal-ammoniac, crystallises in fine rhombohedral prisms.

Rhodium Oxides.—Rhodium forms three oxides, containing RhO, Rh_2O_3, RhO_2.

The *monoxide*, RhO, is formed with incandescence, when the hydrated sesquioxide, $Rh_2O_3,3H_2O$, is heated in a platinum crucible. It is a dark grey substance, perfectly indifferent to acids.

The *sesquioxide*, or *Rhodic oxide*, Rh_2O_3, obtained by heating the nitrate, is a grey porous mass, with metallic iridescence; insoluble in acids, easily reduced by hydrogen.

The *trihydroxide* or *Rhodic Hydroxide*, $Rh_2(OH)_6$, is formed as a black gelatinous precipitate on heating a solution of sodio-rhodic chloride with caustic potash. When dry it forms a heavy dark-brown metallically lustrous mass having a conchoïdal fracture. It is scarcely attacked by acids. A solution of sodio-rhodic chloride treated with potash in the cold, becomes opaque, and after some time deposits thin lemon-yellow crystals of the hydrate $Rh_2(OH)_6$, $2H_2O$, which dissolves readily in acids, and when moist in caustic potash.

The *dioxide*, RhO_2, obtained by fusing pulverised rhodium or the sesquioxide with nitre and potash, and digesting the fused mass with nitric acid, to dissolve out the potash, is a dark-brown substance

insoluble in acids. When chlorine is passed into a solution of rhodic pentahydrate, $Rh_2O_3,5H_2O$, a black-brown gelatinous precipitate of the trihydrate, $Rh_2O_3,3H_2O$, is formed at first; but this compound gradually loses its gelatinous consistence, becomes lighter in colour, and is finally converted into a green hydrate of the dioxide, $RhO_2,2H_2O$. The alkaline solution at the same time acquires a deep violet-blue colour.

The *tetrahydroxide*, $Rh(OH)_4$, separates, on passing chlorine for a long time into an alkaline solution of the trihydroxide, with occasional addition of potash, in the form of a green powder, the liquid at the same time assuming a blue or violet tint. The green powder dissolves in hydrochloric acid, yielding a blue solution gradually changing to dark red, with evolution of chlorine. The violet-blue solution probably contains the potassium salt of a *rhodic acid*, which latter separates after some time as a blue powder, and is converted on drying into the tetrahydroxide.

Rhodic Sulphate, $Rh_2(SO_4)_3 12H_2O$, formed by oxidising the sulphide with nitric acid, is a yellowish-white crystalline mass. *Potassio-rhodic sulphate*, $RhK_3(SO_4)_3$, is a reddish-yellow crystalline powder, formed by adding sulphuric acid to a solution of rhodium and potassium chloride.

Ammoniacal Rhodium Compounds. — An *ammonio-chloride*, $(NH_3)_{10}Rh_2Cl_6$, or $\begin{matrix} Cl_2Rh—(NH_3)_5—Cl \\ | \\ Cl_2Rh—(NH_3)_5—Cl \end{matrix}$, is obtained as a yellow crystalline powder on mixing a dilute solution of rhodium and ammonium chloride with excess of ammonia, and leaving the filtered solution to evaporate. The corresponding oxide, $(NH_3)_{10}Rh_2O_3$, obtained by heating the chloride with silver oxide, is a strong base, from which the sulphate and oxalate may be obtained in crystalline form.

Rhodic salts are, for the most part, rose-coloured, and exhibit in solution the following reactions: with *hydrogen sulphide* and *ammonium sulphide*, a brown precipitate of rhodic sulphide, insoluble in excess of ammonium sulphide: with soluble *sulphites*, a pale yellow precipitate, affording a characteristic reaction; with *potash* a yellow precipitate of rhodic oxide, soluble in excess; with *ammonia* and with *alkaline carbonates*, a yellow precipitate after a while. No precipitate with alkaline chlorides or mercuric cyanide. *Zinc* precipitates metallic rhodium.

An alloy of steel and rhodium in equal parts has a density of 9·176, a very fine colour and lustre for metallic mirrors, and does not tarnish in the air.

IRIDIUM.

Symbol, Ir. Atomic weight, 196·7.

When crude platinum is dissolved in nitro-muriatic acid, a small quantity of a grey scaly metallic substance usually remains behind, having altogether resisted the action of the acid: this is a native alloy of iridium and osmium, called *osmiridium* or *iridosmine;* it is reduced to powder, mixed with an equal weight of dry sodium chloride, and heated to redness in a glass tube, through which a stream of moist chlorine gas is transmitted. The further extremity of the tube is connected with a receiver containing solution of ammonia. The gas, under these circumstances, is rapidly absorbed, iridium chloride and osmium chloride being produced: the former remains in combination with the sodium chloride; the latter, being a volatile substance, is carried forward into the receiver, where it is decomposed by the water into osmic and hydrochloric acids, which combine with the alkali. The contents of the tube when cold are treated with water, by which the iridium and sodium chloride is dissolved out; this is mixed with an excess of sodium carbonate, and evaporated to dryness. The residue is ignited in a crucible, boiled with water, and dried; it then consists of a mixture of ferric oxide and a combination of iridium oxide with soda: it is reduced by hydrogen at a high temperature, and treated successively with water and strong hydrochloric acid, by which the alkali and the iron are removed, while metallic iridium is left in a finely divided state. By strong pressure and exposure to a white heat, a certain degree of compactness may be communicated to the metal.*

Iridium is a white brittle metal, fusible with great difficulty before the oxy-hydrogen blow-pipe. Deville and Debray, by means of their powerful oxy-hydrogen blast furnace, have fused it completely into a pure white mass, resembling polished steel, brittle in the cold, somewhat malleable at a red heat, and having a density equal to that of platinum, viz., 21·15. By moistening the pulverulent metal with a small quantity of water, pressing it tightly, first between filtering paper, then very forcibly in a press, and calcining it at a white heat in a forge fire, it may be obtained in the form of a compact, very hard mass, capable of taking a good

* Osmiridium, however, generally contains platinum, ruthenium, and other metals of the same group, which are not effectually separated by the method above described. The complete separation of the several metals of the platinum group has of late years formed the subject of several elaborate investigations, into which the limits of this work will not permit us to enter. (See Watts's Dictionary of Chemistry, iii. 35; iv. 241, 680; v. 101, 124; and Roscoe and Schorlemmer's Treatise on Chemistry, vol. ii. part ii. pp. 390—396 and 438—441.)

polish, but still very porous, and of a density not exceeding 16·0. After strong ignition it is insoluble in all acids, but when reduced by hydrogen at low temperatures, it oxidises slowly at a red heat, and dissolves in nitro-muriatic acid. It is usually rendered soluble by fusing it with nitre and caustic potash, or by mixing it with common salt, or better, with a mixture of the chlorides of potassium and sodium, and igniting it in a current of chlorine, as above described.

Iridium forms three series of compounds, namely, the hypo-iridious compounds, in which it is bivalent, as $IrCl_2$, IrO; the iridious compounds, in which it is trivalent or quadrivalent, *e.g.*, $IrCl_3$ or $Ir_2Cl_6 = Cl_3Ir.IrCl_3$; and the iridic compounds, in which it is also quadrivalent, as in $IrCl_4$, IrO_2, &c.* It forms also a trioxide, IrO_3, in which it appears to be sexvalent.

Chlorides.—Iridium appears to form three chlorides, but only two of them—namely, the trichloride and tetrachloride—have been obtained in definite form.

The *dichloride*, $IrCl_2$, is not known in the separate state, but appears to exist in certain double salts, called *hypochloriridites*.

The *trichloride*, or *Iridious chloride*, $IrCl_3$, or Ir_2Cl_6, is prepared by strongly heating iridium with nitre, adding water and enough nitric acid to saturate the alkali, warming the mixture, and then dissolving the precipitated hydrate of the sesquioxide in hydrochloric acid; it forms a dark yellowish-brown solution. This substance combines with other metallic chlorides, forming compounds called *iridoso-chlorides* or *chloriridites*, which may be prepared by reducing the corresponding chloriridiates with sulphurous acid, hydrogen sulphide, or potassium ferrocyanide. Claus has obtained the compounds $IrCl_3,3NH_4Cl,3H_2O$, $IrCl_3,3KCl,3H_2O$, and $IrCl_3,3NaCl$, $12H_2O$. They are olive-green pulverulent salts, soluble in water.

The *tetrachloride*, or *Iridic chloride*, $IrCl_4$, is obtained in solution by dissolving very finely divided iridium, or one of its oxides, or the trichloride, in nitro-muriatic acid, and heating the liquid to the boiling-point. On evaporating the solution, it remains in the form of a black, deliquescent, amorphous mass, translucent with dark-red colour at the edges; soluble, with reddish-yellow colour, in water. It unites with alkaline chlorides, forming compounds called *iridiochlorides* or *chloriridiates*, analogous in composition to the chloroplatinates. The *ammonium salt*, $(NH_4)_2IrCl_6,H_2O$, and the *potassium salt*, K_2IrCl_6, or $2KCl,IrCl_4$, are formed, as dark-brown crystalline

* A hexchloride, $IrCl_6$, was said by Berzelius to be obtained in combination with potassium chloride by fusing iridosmine with nitre, distilling the product with nitro-muriatic acid, and treating the residue with successive portions of water; but, according to Claus, the salt formed was really a ruthenium compound, having been prepared by Berzelius from iridosmine containing ruthenium.

precipitates, on mixing the solutions of the component chlorides. The potassium salt may also be prepared by passing chlorine over a gently ignited and finely divided mixture of iridium with potassium chloride. It is soluble in boiling water, and crystallises in black octohedrons, yielding a red powder. The *sodium salt*, Na_2IrCl_6, $6H_2O$, prepared like the potassium salt, forms easily soluble black tables and prisms, isomorphous with the corresponding platinum salt.

Iodides.—Iridium forms three iodides, IrI_2, IrI_3, and IrI_4, analogous to the chlorides, and yielding similar double salts with the iodides of the alkali-metals.*

Oxides.—Iridium forms three oxides, IrO, Ir_2O_3, and IrO_2. The *monoxide*, or *hypoiridious oxide*, IrO, is but little known. It is obtained by precipitating an alkaline hypochloriridite with caustic alkali in an atmosphere of carbon dioxide; but on exposure to the air it is quickly converted into a higher oxide.

The *sesquioxide*, or *Iridious oxide*, Ir_2O_3, was formerly regarded as the most easily formed and most stable of the oxides of iridium; but, according to Claus, it has a great tendency to take up oxygen and pass to the state of dioxide. It may be prepared by gently igniting a mixture of potassium chloriridite ($K_6Ir_2Cl_3$) with sodium carbonate in an atmosphere of carbon dioxide; on treating the product with water, the sesquioxide remains in the form of a black powder insoluble in acids. The *trihydroxide* or *Iridious Hydroxide*, $Ir_2(OH)_6$, is prepared like the corresponding rhodium compound, which it closely resembles.

Iridious oxide unites with bases, forming salts which may be called *iridites*. A solution of a chloriridite in excess of lime-water deposits, after standing for some time out of contact of air, a dirty yellow precipitate containing $3CaO,Ir_2O_3$.

The *dioxide* or *Iridic oxide*, IrO_2, is a black powder obtained by heating the tetrahydroxide in a current of carbon dioxide. It is insoluble in acids.—The *Tetrahydroxide* or *Iridic Hydroxide*, $Ir(OH)_4$, formed by oxidation of iridious hydroxide in the air, or by precipitating the tetrachloride with an alkali, is a heavy indigo-blue powder, almost insoluble in dilute sulphuric and nitric acids, but dissolving slowly in hydrochloric acid. The indigo-blue solution when heated turns green, and afterwards brown.

Iridium, like the other platinum metals, shows but little tendency to form oxygen salts. The oxides dissolve in acids, but no definite salts are obtained in this way. The solution of iridic oxide in sulphuric acid has a dark-brown colour, which is not modified by potash in the same manner as that of the dichloride; neither does it yield any blue precipitate on boiling.

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* Offler, Ueber die Iodverbindungen des Iridiums. Göttingen, 1857.

The only definite oxygen-salts of iridium that have been obtained are an iridious sulphite and double salts containing sulphurous and dithionic acids.

Iridious Sulphite, $Ir_2(SO_3)_3,6H_2O$, is formed on passing sulphur dioxide into water, holding the trioxide in suspension, and separates from solution on evaporation as a yellow crystalline precipitate.

Hypo-iridoso-potassic Sulphite, $K_6Ir_2(SO_3)_4$, is obtained as a white crystalline powder, when the mother-liquor obtained in preparing potassium chloriridite by passing sulphurous oxide through a solution of the chloriridate, is evaporated to a small bulk.

Sulphides.—Three sulphides of iridium are known, analogous to the first three oxides above described. The *sesquisulphide* and *disulphide* are obtained as brown-black precipitates by treating the solutions of the trichloride and tetrachloride respectively with hydrogen sulphide. The *monosulphide* is a greyish-black substance obtained by decomposing either of the higher sulphides in a close vessel.

Ammoniacal Compounds of Iridium.—The *chlorides of iridosammonium* and *iridosodiammonium*, $Ir(NH_3Cl)_3$ and $Ir[NH_2(NH_4)Cl]_3$, together with the corresponding sulphates, are prepared like the platinous compounds of analogous composition, which they also resemble in their properties. The *nitratochloride*, $Ir<\begin{matrix}NH_2(NH_4)NO_3\\NH_2(NH_4)Cl\end{matrix}$, is formed by heating the chloride, $Ir(NH_3Cl)_3$, with strong nitric acid. *Iridiodiammonium chloride*, $Cl_2Ir[NH_2(NH_4)Cl_2$, is obtained as a violet precipitate by treating the nitrate just mentioned with hydrochloric acid.*

The compound $10NH_3,Ir_2Cl_6$, analogous to the rhodium-compound above described (p. 563), but having no analogue in the platinum series, is obtained as a flesh-coloured crystalline powder by prolonged digestion of ammonium chloriridate with warm aqueous ammonia. The corresponding carbonate, nitrate, and sulphate have also been prepared.†

Iridic solutions (containing the dioxide or tetrachloride) are of a dark brown-red colour; iridious solutions (containing the sesquioxide or trichloride) have an olive-green colour. The characters of an iridic solution are best observed with sodium chloriridate, all the other iridic compounds being but slightly soluble.

Iridic solutions give with *ammonium* or *potassium chloride* a crystalline precipitate of ammonium or potassium chloriridate, which is distinguished from the corresponding platinum precipitate by its

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* Skoblikoff, Ann. Ch. Pharm., lxxxiv. 275.

† Claus, Beiträge zur Chemie der Platinmetalle. Dorpat, 1854.

TABLE IV.

WEIGHTS AND MEASURES.

480	grains Troy	=	1 oz. Troy.
437·5	„	=	1 oz. Avoirdupois.
7000	„	=	1 lb. Avoirdupois.
5760	„	=	1 lb. Troy.

The imperial gallon contains of water at 62° F. (16⅔° C.) 70,000 grains
The pint ($\frac{1}{8}$ of gallon) . . . . . 8,750 „
The fluid ounce ($\frac{1}{20}$ of pint) . . . . . 437·5 „

The pint equals 34·56 cubic inches.

A soluble dichloride is formed by passing sulphydric acid gas into a solution of the trichloride, a brown sulphide being then precipitated, and the solution acquiring a fine blue colour.

The *trichloride*, or *Ruthenious chloride*, $RuCl_3$, prepared by precipitating a solution of potassic ruthenite with an acid, dissolving the precipitated black oxide in hydrochloric acid, and evaporating, is a yellow-brown, crystalline, very deliquescent mass, becoming dark-green and blue at certain points when strongly heated. It dissolves easily in water and in alcohol, leaving a small quantity of a yellow insoluble salt.

The concentrated solution of ruthenious chloride, mixed with concentrated solutions of the chlorides of potassium and ammonium, yields the double salts, $K_4Ru_2Cl_{10}$ and $(NH_4)_2Ru_2Cl_{10}$, in the form of crystalline precipitates, with violet iridescence, very slightly soluble in water, insoluble in alcohol.

The *tetrachloride*, or *Ruthenic chloride*, $RuCl_4$, is known only in its double salts. The *potassium salt*, or $K_2Ru^{IV}Cl_6$, is prepared by mixing a solution of ruthenic hydroxide in hydrochloric acid with potassium chloride, and evaporating to the crystallising point. It is brown, with rose-coloured iridescence, very soluble in water, but insoluble in alcohol. The *ammonium salt*, $(NH_4)_2RuCl_6$, is prepared like the potassium salt, which it closely resembles.

Oxides.—Ruthenium forms six oxides, viz., RuO, Ru_2O_3, RuO_2, RuO_3, Ru_2O_7, and RuO_4, the fourth and fifth, however, being known only in combination.

The *monoxide*, RuO, obtained by calcining the dichloride with sodium carbonate in a current of carbon dioxide, and washing the residue with water, has a dark-grey colour and metallic lustre; is not acted upon by acids; but is reduced by hydrogen at ordinary temperatures.—The *sesquioxide*, or *Ruthenious oxide*, Ru_2O_3, is a bluish-black powder, formed by heating the metal in the air. The corresponding hydroxide, $Ru(OH)_3$, is obtained by precipitating ruthenious chloride with an alkaline carbonate, as a blackish-brown substance which dissolves with yellow colour in acids. The *dioxide*, or *Ruthenic oxide*, RuO_2, is a black-blue powder, obtained by roasting the disulphide. *Ruthenic Hydroxide*, $Ru(OH)_4$, is obtained as a gelatinous precipitate by decomposing potassium chlororutheniate with sodium carbonate.—The *trioxide*, RuO_3, commonly called *ruthenic acid*, is known only as a potassium salt, which is obtained by igniting ruthenium with caustic potash and nitre: it forms an orange-yellow solution.—The *oxide*, Ru_2O_7, called *Ruthenium Peroxide*, is not known in the free state, neither has the corresponding acid "per-ruthenic acid" been obtained; but the potassium salt is formed by the action of chlorine on potassium ruthenate, and separates from the resulting dark-green solution in black lustrous rhombic pyramids, isomorphous with potassium permanganate. The blackish-green solution soon turns yellow, being resolved into potassium ruthenate and the following oxide.—The *tetroxide*, RuO_4,

dichloride, then a red sublimate of the tetrachloride. The *dichloride* or *hypo-osmious chloride*, dissolves in water with dark violet-blue colour. It is likewise formed by the action of reducing agents on either of the higher chlorides, into which, on the other hand, it is easily converted by oxidation. The addition of potassium chloride renders it more stable, by forming a double salt. The *trichloride* has not been isolated, but is contained in the solution obtained by treating the sesquioxide with hydrochloric acid. It forms double salts with alkaline chlorides. The *potassium salt*, $K_6Os_2Cl_{12}6H_2O$, is produced, together with potassium chlorosmate, when a mixture of pulverised osmium and potassium chloride is ignited in chlorine gas; it forms dark red-brown crystals.

The *tetrachloride*, or *Osmic chloride*, $OsCl_4$, is the red compound which constitutes the principal part of the product obtained by igniting osmium in chlorine gas. It dissolves with yellow colour in water and alcohol, and is decomposed quickly in dilute solution, more slowly in presence of hydrochloric acid or metallic chlorides, yielding a black precipitate of osmic oxide, and a solution of osmium tetroxide in hydrochloric acid.

Osmic chloride unites with the chlorides of the alkali-metals, forming salts sometimes called osmiochlorides, or chlorosmates. From the solutions of these salts *hydrogen sulphide* and *ammonium sulphide* slowly precipitate a yellow-brown sulphide, insoluble in alkaline sulphides; *silver nitrate* forms an olive-green, *stannous chloride* a brown precipitate. *Tannic acid*, on heating, produces a blue colour, but no precipitate; *potassium ferrocyanide*, first a green, then a blue colour; *potassium iodide*, a deep purple-red colour. *Potash* gives a black, *ammonia* a brown precipitate, slowly in the cold, immediately on boiling. Metallic *zinc* and *sodium formate* throw down metallic osmium.

Sodium osmiochloride, Na_2OsCl_6, prepared by heating a mixture of osmium sulphide and sodium chloride in a current of chlorine, crystallises in orange-coloured rhombic prisms, an inch long, easily soluble in water and in alcohol. The *potassium* and *ammonium salts*, of analogous composition, are obtained as red-brown crystalline precipitates on adding sal-ammoniac or potassium chloride to the solution of the sodium salt.

Oxides.—Osmium forms five oxides analogous to those of ruthenium. The *monoxide*, or *Hypo-osmious oxide*, OsO, is obtained by igniting hypo-osmious sulphite in a stream of carbonic acid gas; also as a blue-black hydrate, by heating the same salt with strong potash solution in a closed vessel. *Hypo-osmious sulphite*, $OsSO_3$ or OsO,SO_2, is a black-blue salt, produced by mixing the aqueous solution of osmium tetroxide with sulphurous acid.—The *sesquioxide* or *Osmious oxide*, Os_2O_3, is obtained by heating either of the double salts of the trichloride with sodium carbonate in a stream of carbonic acid gas. It is a black powder, insoluble in acids. The

hydroxide, obtained by precipitation, has a dirty brown-red colour, is soluble in acids, but does not yield pure salts.

The *dioxide*, or *Osmious oxide*, OsO_2, is obtained as a black insoluble powder, by heating potassium osmiochloride with sodium carbonate in a stream of carbonic acid gas, or in copper-red metallic shining lumps, by heating the corresponding hydroxide. *Osmious hydroxide*, or *Osmious acid*, $Os(OH)_4$, is obtained by precipitating a solution of potassium osmio-chloride with potash, at the boiling heat, or in greater purity by mixing a solution of potassium osmate, K_2OsO_4, with dilute nitric acid according to the equation,

$$2K_2OsO_4 + 4HNO_3 = Os(OH)_4 + OsO_4 + 4KNO_3.$$

The *trioxide*, OsO_3, and the corresponding hydroxide or *Osmic acid*, H_2OsO_4, are not known, osmium in this respect resembling manganese; but the osmates of alkali-metals are formed by the action of reducing agents in presence of alkalis on the tetroxide. The *potassium salt*, $K_2OsO_4,2H_2O$, is a rose-coloured crystalline powder.

The *tetroxide*, OsO_4, commonly called *Osmic acid*, is the volatile strong-smelling compound, formed when osmium or either of its lower oxides is heated in the air or treated with nitric or nitro-hydrochloric acid. It may be prepared by heating osmium in a current of oxygen gas, and condenses in the cool part of the apparatus, in colourless transparent crystals. It melts below 100°, and boils at a temperature a little above its melting point. Its vapour has an intolerably pungent odour, attacks the eyes strongly and painfully, and is excessively poisonous. Osmium tetroxide is dissolved slowly, but in considerable quantity, by water, forming an acid solution. It is a powerful oxidising agent, decolorising indigo-solution, separating iodine from potassium iodide, converting alcohol into aldehyde and acetic acid, &c. It dissolves in alkalis, forming yellow-red solutions, which are inodorous when cold, but when heated, give off the tetroxide and free oxygen, leaving a residue of alkaline osmite.

Sulphides.—Osmium burns in sulphur-vapour. Five sulphides of osmium are said to exist, analogous to the oxides, the first four being produced by decomposing the corresponding chlorides with hydrogen sulphide, and the tetrasulphide by passing that gas into a solution of the tetroxide. The last is a sulphur-acid, perfectly soluble in water, whereas the others are sulphur-bases, slightly soluble in water, and forming deep yellow solutions.

Ammoniacal Osmium Compounds.—A cold solution of potassium osmite, mixed with sal-ammoniac, yields a yellow crystalline precipitate, consisting, according to Claus, of *hydrated osmammonium chloride*, $Os(NH_3Cl)_2$. An aqueous solution of the tetroxide treated with ammonia, yields a brown-black powder, consisting of $N_2H_8OsO_3$, or $O{=}Os{<}\begin{matrix}NH_3\\NH_3\end{matrix}{>}O + H_2O$.

Table VII.

Weight of one Cubic Centimeter of Atmospheric Air, in Grams, at different Temperatures, for every 5 Degrees from 0° to 300°C. at 760 mm.

		Difference.			Difference.
0°	0·001293		155°	0·000824	
		23			9
5	0·001270		160	0·000815	
		22			9
10	0·001248		165	0·000806	
		22			9
15	0·001226		170	0·000797	
		21			9
20	0·001205		175	0·000788	
		20			9
25	0·001185		180	0·000779	
		20			9
30	0·001165		185	0·000770	
		19			8
35	0·001146		190	0·000762	
		18			8
40	0·001128		195	0·000754	
		17			8
45	0·001111		200	0·000746	
		17			8
50	0·001094		205	0·000738	
		17			8
55	0·001077		210	0·000730	
		17			8
60	0·001060		215	0·000722	
		16			7
65	0·001044		220	0·000715	
		15			7
70	0·001029		225	0·000708	
		15			7
75	0·001014		230	0·000701	
		14			7
80	0·001000		235	0·000694	
		14			7
85	0·000986		240	0·000687	
		14			7
90	0·000972		245	0·000680	
		13			6
95	0·000959		250	0·000674	
		13			6
100	0·000946		255	0·000668	
		13			6
105	0·000933		260	0·000662	
		12			6
110	0·000921		265	0·000656	
		12			6
115	0·000909		270	0·000650	
		11			6
120	0·000898		275	0·000644	
		11			6
125	0·000887		280	0·000638	
		11			6
130	0·000876		285	0·000632	
		11			6
135	0·000865		290	0·000626	
		11			5
140	0·000854		295	0·000621	
		10			5
145	0·000844		30	0·000616	
		10			
150	0·000834				

The column of Differences is intended to facilitate the calculation of the intermediate values. Thus to find the weight of 1 cub. cent. of air for 52°, we must deduct from the weight for 50°, two-fifths of the difference (17) between this and the number for 55 degrees: thus

Weight of 1 cub. cent. of air at 50°	=	0·001094
Deduct $\frac{2}{5}$ of 17	=	7
Weight of 1 cub. cent. of air at 55°	=	0·001087

TABLE VIII.

FOR THE CALCULATION OF $\frac{1}{1+0{\cdot}00367t}$. (*See page* 70.)

t		t		t		t		t	
1	0·99634	31	0·89785	61	0·81708	91	0·74964	121	0·69249
2	0·99271	32	0·89490	62	0·81464	92	0·74758	122	0·69073
3	0·98911	33	0·89197	63	0·81221	93	0·74554	123	0·68899
4	0·98553	34	0·88906	64	0·80979	94	0·74351	124	0·68725
5	0·98198	35	0·88617	65	0·80740	95	0·74148	125	0·68552
6	0·97845	36	0·88330	66	0·80501	96	0·73947	126	0·68380
7	0·97495	37	0·88044	67	0·80264	97	0·73747	127	0·68209
8	0·97148	38	0·87761	68	0·80068	98	0·73548	128	0·68038
9	0·96803	39	0·87479	69	0·79794	99	0·73350	129	0·67869
10	0·96460	40	0·87199	70	0·79561	100	0·73153	130	0·67700
11	0·96120	41	0·86921	71	0·79329	101	0·72957	131	0·67532
12	0·95782	42	0·86645	72	0·79099	102	0·72762	132	0·67365
13	0·95446	43	0·86370	73	0·78870	103	0·72568	133	0·67199
14	0·95113	44	0·86097	74	0·78642	104	0·72376	134	0·67034
15	0·94782	45	0·85826	75	0·78416	105	0·72184	135	0·66870
16	0·94454	46	0·85556	76	0·78191	106	0·71993	136	0·66706
17	0·94127	47	0·85289	77	0·77967	107	0·71803	137	0·66543
18	0·93803	48	0·85022	78	0·77745	108	0·71615	138	0·66380
19	0·93482	49	0·84758	79	0·77523	109	0·71427	139	0·66219
20	0·93162	50	0·84495	80	0·77304	110	0·71240	140	0·66059
21	0·92844	51	0·84234	81	0·77085	111	0·71055	141	0·65899
22	0·92529	52	0·83974	82	0·76867	112	0·70870	142	0·65740
23	0·92216	53	0·83716	83	0·76651	113	0·70686	143	0·65582
24	0·91905	54	0·83460	84	0·76436	114	0·70503	144	0·65424
25	0·91596	55	0·83205	85	0·76222	115	0·70321	145	0·65268
26	0·91289	56	0·82952	86	0·76010	116	0·70140	146	0·65112
27	0·90984	57	0·82700	87	0·75798	117	0·69960	147	0·64957
28	0·90682	58	0·82450	88	0·75588	118	0·69781	148	0·64802
29	0·90381	59	0·82201	89	0·75379	119	0·69603	149	0·64648
30	0·90082	60	0·81954	90	0·75171	120	0·69425	150	0·64495

Table II.

Baumé's Hydrometer for Liquids Lighter than Water.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
10	1·000	27	0·896	44	0·811
11	0·993	28	0·890	45	0·807
12	0·986	29	0·885	46	0·802
13	0·980	30	0·880	47	0·798
14	0·973	31	0·874	48	0·794
15	0·967	32	0·869	49	0·789
16	0·960	33	0·864	50	0·785
17	0·954	34	0·859	51	0·781
18	0·948	35	0·854	52	0·777
19	0·942	36	0·849	53	0·773
20	0·936	37	0·844	54	0·768
21	0·930	38	0·839	55	0·764
22	0·924	39	0·834	56	0·760
23	0·918	40	0·830	57	0·757
24	0·913	41	0·825	58	0·753
25	0·907	42	0·820	59	0·749
26	0·901	43	0·816	60	0·745

These two tables are on the authority of Francœur: they are taken from the *Handwörterbuch der Chemie* of Liebig, Poggendorff, and Wöhler. Baumé's hydrometer is very commonly used on the Continent, especially for liquids heavier than water. For lighter liquids the hydrometer of Cartier is often employed in France. Cartier's degrees differ but little from those of Baumé.

In the United Kingdom, Twaddell's hydrometer is a good deal used for dense liquids. This instrument is so graduated that the real specific gravity can be deduced by an extremely simple method from the degree of the hydrometer; namely, by multiplying the latter by 5, and adding 1000; the sum is the specific gravity, water being 1000. Thus 10° Twaddell indicates a specific gravity of 1050, or 1·05; 90° Twaddell, 1450, or 1·45.

In the Customs and Excise, Sykes's hydrometer is used.

TABLE III.

ABSTRACT

OF REGNAULT'S TABLE OF THE MAXIMUM TENSION OF WATER-VAPOUR AT DIFFERENT TEMPERATURES, EXPRESSED IN MILLIMETERS OF MERCURY.

Temperature.	Tension, millimeters.	Temperature.	Tension, millimeters.
−32° C.	0·320	100° C.	760·000
30	0·386	105	906·410
25	0·605	110	1075·370
20	0·927	115	1269·410
15	1·400	120	1491·280
10	2·093	125	1743·880
5	3·113	130	2030·280
0	4·600	135	2353·730
+ 5	6·534	140	2717·630
10	9·165	145	3125·55
15	12·699	150	3581·23
20	17·391	155	4088·56
25	23·550	160	4651·62
30	31·548	165	5274·54
35	41·827	170	5961·66
40	54·906	175	6717·43
45	71·391	180	7546·39
50	91·982	185	8453·23
55	117·478	190	9442·70
60	148·791	195	10519·63
65	186·945	200	11688·96
70	233·093	205	12955·66
75	288·517	210	14324·80
80	354·643	215	15801·33
85	433·041	220	17390·36
90	525·450	225	19097·04
95	633·778	230	20926·40

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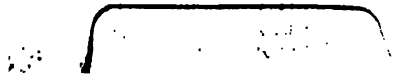
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